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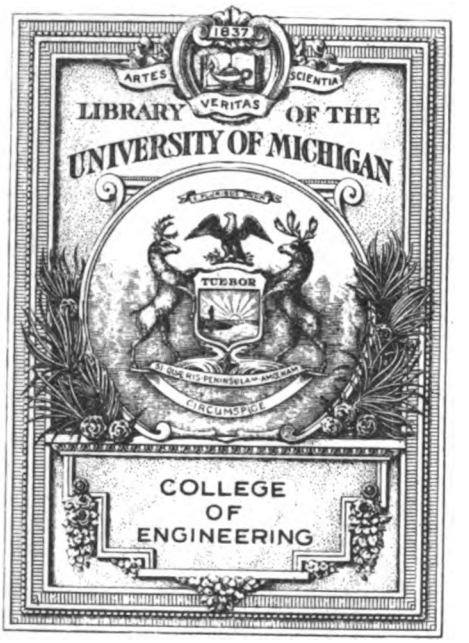

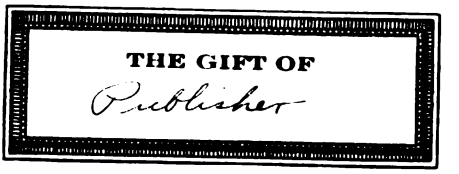

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FRASER M. MOFFAT
President Tanners' Council

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CORRECTION

The Chairman of the Committee on Sampling of Leather and Its Preparation for Analysis wishes to call attention to an error in the report of the Committee as published in the August, 1921 issue. The numbering of the samples in the tables on pages 399 and 401 were not changed to conform with the general scheme. They should be as follows:—

Table on Page 399

Sample No.	2	4	11	18	24	26	31	34
Should be	3	5	13	20	26	28	36	33

Table on Page 401

Sample No.	1	2	3	4	11	18	24	26	31	34
Should be	2	3	4	5	13	20	26	28	36	33

WILHELM EITNER

1843-1921

Wilhelm Eitner, the founder of *Der Gerber,* one of the early pioneers in our field of endeavor, whose entire life was given up to it and who made many valuable contributions to the advancement of our knowledge, died on October 13, 1921. As a tribute and in fitting commemoration we give in full a translation of an obituary as it appears in *Der Gerber* for November 10, 1921.

"With Wilhelm Eitner, tanning science and leather manufacture loses one of its best technical men, one who enjoyed renown in foreign countries as well as in Austria; who, indeed, was recognized throughout the world as a technical authority. Eitner was born on the 26th of January, 1843, in Iglau, the son of a cloth maker. He attended the preparatory school (Unterrealschule) at that place, then completed his studies in the Oberrealschule in Vienna, following which he studied chemistry in the Technical High School at that place.

"After the completion of his studies at the age of 20 he began as chemist for the L. Jellinek Glove Works in Prague-Lieben. Later he entered the leather works of the former A. H. Suesz and Sons in Vienna, and after five years accepted a post with the firm Ludw. B. Goldschmidt in Prague-Vysehrad. In all of these works where he could turn his theoretical knowledge to

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good account, he diligently assembled many practical processes. In 1872 he accepted the position of a vice-director in the Slouper Aktienlederfabrik.

"In 1874, Eitner was called to Vienna to establish and direct a state research and instruction institute, where he inaugurated an extremely zealous and successful activity. During his activity of almost forty years there, he developed a long series of able technologists of whom many occupy prominent posts, and many of them have already died. Of the deceased may be mentioned: Fr. Andreasch, Assistant of the Vienna Versuchsanstalt; Valdemar Bögh, Director of the Danish Versuchsanstalt in Copenhagen; Franz Kathreiner, Cheif Chemist of the Lederfabrik in Worms; Karl Sadlon, Leather Works Director. Among those active to-day are: Vittorio Casaburi, Director of the Royal Research Institute in Naples; Dr. Edmund Stiasny, Professor of the High School and Director of the Versuchsanstalt in Darmstadt; Jos. Schneider, Professor at the Czech Technical High School in Prague; Marko Smaic, Director, and J. Wladika, Professor of the Vienna Versuchsanstalt and many others.

"In the same year (1874) Eitner with his cousin Prof. Ignaz Eitner founded the technical journal *Der Gerber* which soon won its renown, since it brought more excellent treatises of technical and scientific contents than any other of that time. The volumes of *Der Gerber* are still to-day of so great a value that the International Association of Leather Trades Chemists are thinking of reprinting the older ones.

"Eitner with his assistants and associates has performed an enormous work in the forty years; he has carried out fundamental investigations in tanning chemistry and has assembled and published an extraordinarily large amount of practical knowledge. For that reason Eitner was consulted by hundreds of tanners and leather manufacturers, and also was active in the service of the State as assistant counsellor of customs, permanent member of the Patent office and as expert for numerous commissions. It was also for this reason that he was distinguished by the bestowal of the title of a Regierungsrat (member of an official council), and the bestowal of the Order of Kaiser-Franz-Josef, otherwise he was not honoured to the extent he merited.

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"As the independent Research Institute was incorporated under the chemical-technical direction of the State Industrial School and Eitner would be subordinated to a much younger director, wholly unskilled in leather technology, at the end of 1909 he took a long leave of absence from which he never returned to his beloved Research Institute. On the 10th of April, 1913, he resigned his office.

"He remained associated with *Der Gerber* longer. At the end of the year 1910 he gave up the post as its editor but still published many valuable treatises in this journal. Bitter are the words with which he informed his readers and friends of the giving up of this post.

"Until the last year of life Eitner remained active in literature, yet in 1876 he had merely published the work 'The Manufacture of Leather in North America'. He has published all of his other treatises in various journals, the most of them in *Der Gerber*.

"The deceased was restlessly active his entire life. It was not easy to work with the extremely scanty means of the Versuchsanstalt. However, his large technical knowledge, his indefatigable joy in work and exemplary industry made it possible for him to accomplish such truly extraordinary results.

"Still fairly fresh but of advancing age and not untouched by bitter experiences, Eitner peacefully fell asleep on the 13th of October in Kristofen near Neulengbach (North Austria) and was buried in the small church-yard there.

May he rest in peace! Many hundred of his students, many thousand readers of *Der Gerber*, all the technical men of the whole world will remember him with respect and appreciation."

G. W. S.

THE TANNER'S COUNCIL AND THE CHEMIST

By Robert W. Griffith

It is generally conceded by all those who attended the October Meeting of The Tanner's Council, which was held at the Drake Hotel, Chicago, that it was one of the most successful Meetings ever held by the Tanners.

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Certainly there has been no meeting in recent years at which so much attention has been paid to the technical side of the industry whether or no this may account for the success of the meeting. Many of the papers presented have a direct interest for the chemist and it seems desirable therefore to give a brief account of the meetings and papers, insofar as they had this appeal to our Association. It may be remarked in passing that at no recent meeting has so great an interest been shown by the Tanners' Council in the activities of our Association and this well may afford encouragement for the belief that each Association is appreciating more fully how intimately tied together are the interests of both and how essential it is that full and free exchange of thought take place between them.

Of great value from the point of view of industrial reconstruction was the paper contributed by Mr. Fred A. Miller on "Trade Revival," which dealt with the economics of the leather industry, an angle of the situation which the chemist cannot ignore if he is to be efficient in the discharge of his responsibilities. Mr. Miller's survey of the industry was comprehensive and well reasoned and he sought to emphasize that tables and charts depicting leather values meant nothing unless they have a relation to essential commodities in general. That the level of relative values is the hard pan upon which the foundation of reconstructed industry must rest and that our present job is to expedite the balancing of values and to avail ourselves of the present opportunity to make the necessary preparation for the resumpton of business, which will inevitably occur.

As an authority on leather manufacture, Mr. Fred A. Vogel, needs no introduction to the American leather chemist. Himself trained in the technicalities of the tanning industry and supplemented by a wide experience in the practical operation of a number of tanneries, producing a large variety of leathers, there is no one better qualified to speak on the subject of "Modernizing the Tanning Industry," with which Mr. Vogel held the interest of his audience. The paper was a bold presentation of the present situation in the tanning industry. Mr. Vogel's survey covered the subject of plant location or relocation, plant equipment, personnel and merchandising. He advocated a new alignment of the industry with reference to the raw material supply and the

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market for leather. The installation of labor saving machinery as a prime necessity, and that the greatest efficiency is based upon the confidence of labor in the management. One of the essentials to a properly equipped plant organization is the chemist, and of his part in the scheme Mr. Vogel says: "The chemist is ever more finding his place in our midst and I am sure with the many prominent chemical minds now engaging in our industry, our future will and must be greater. The Tanning School for the trade chemist is one of our greatest needs, so that we can develop both practice and theory side by side."

From the point of view of the chemist a most delightful and interesting paper was that read by Mr. Van A. Wallin, on "The Gentle Art of Tanning." The title might suggest a profound exposition of the tanning process with all its exacting details, but it was nothing so ordinary. Mr. Wallin tells a story of a visit to the Leather Research Laboratory of the Tanner's Council at the University of Cincinnati and recounts the impressions of a layman in a most entertaining way. Mr. Wallin was not one of the early enthusiasts for locating the Research Laboratory at a University, and was frankly skeptical, but after a visit to the Laboratory at Cincinnati, he became, like the man in Oliver Goldsmith's poem, "Who came to scoff, but remained to pray." Mr. Wallin's visit not only resulted in a most enthusiastic endorsement of the purpose of the Leather Research Laboratory, but it inspired him to profound thought on the fundamentals of our complex industry, and in this respect it is to be hoped that Mr. Wallin's example will be emulated by an increasing number of members of the tanning industry.

If quiet persistence and everlasting stick-to-it-ness are the essentials to success, then Mr. Louis J. Robertson, who has so long championed the cause of the Tanning School, is bound to win. For some years Mr. Robertson's path has been beset with difficulties and delays, but his enthusiasm for the Tanning School does not seem to wane. At this meeting of the Tanner's Council Mr. Robertson was ably assisted by Dr. Harrison Howe, of the National Research Council, in presenting a very comprehensive plan for the education of students in the industry. Dr. Howe, in a most interesting talk, unfolded the plan which he submitted for the consideration of the Tanner's Council and which was proposed

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by the National Research Council after a very exhaustive study of the subject had been undertaken by that body without any expense to the Tanners and from an entirely independent point of view. The plan has for its purpose the introduction of better trained men into the tanning industry and is based upon evidence that an industry conducted upon scientific lines attracts a better type of workmen than where there is no opportunity to use even such scientific knowledge as may exist. The plan contemplates the training of two distinct classes of men, first, the actual tannery operatives or craftmen, and second, engineers or tannery executives. The instruction of the craftmen is to be directed with the object of giving the men a better understanding of the purpose of their daily tasks and to enable them to receive promotion to higher rank in the industry. For this purpose it is suggested that a miniature tannery be located at Pratt Institute and that the courses in practical instruction should be short and intensive. The Engineers would be recruited from those who have the inclination and necessary qualifications, and it is proposed that the center of their instruction should be at the University of Cincinnati, and that this instruction would be on the so-called "co-operative plan." This plan permits the students, who work in pairs, to alternate between actual tannery work in a neighboring plant, and their study at the University. The University of Cincinnati is the pioneer in educational courses along these lines and the scheme has proved highly successful. From the ranks of the Engineers the men who have a capacity for higher branches of research work, will be recruited, and it is proposed that such men be granted fellowships by the Tanner's Council. The scheme as outlined by Dr. Howe is well considered from every angle of the situation and it is to be hoped that it will become the basis for a much needed activity on the part of the Tanner's Council.

It is not often that the leather chemists have an opportunity to state their case to an assembly of tanners, but the opportunity occurred at this meeting of the Tanner's Council and was taken full advantage of by our President, Mr. Fritz H. Small. In a speech which was exceedingly well delivered, the program of the American Leather Chemists Association activities was set forth in most happy phraseology and conveyed the thought and purpose of the chemist in a clear, and interesting way, which could

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not have failed to have been appreciated and understood by any layman who was privileged to hear it. Mr Small pleaded for the closest kind of co-operation between the Tanner's Council and the American Leather Chemists Association and emphasized the fact that the two Associations were necessary to each other for the carrying out of their common purpose. He congratulated the Tanners on their vision in the establishment of the Leather Research Laboratory at the University of Cincinnati, and very clearly, but briefly outlined the functions of this Laboratory and pointed out its tremendous potential possibilities, bespeaking on behalf of the Laboratory their sturdy and patient support in full confidence that their reward would be great.

While not strictly a chemical problem the activities of the Warble Fly, or more correctly the suppression of those activities, is a subject of immense interest to the tanners all over the world. The ravages of this pest are too well known to tanners to enlarge upon, but regarding methods for eliminating them we have not much information. It was consequently a great pleasure to hear of the scientific work which has been done in this direction in a paper read by Mr. Frank Seymour-Jones, but which was prepared by his father, Mr. Alfred Seymour-Jones, on "The Warble Fly Problem." Mr. Frank Seymour-Jones who has recently graduated from the Leeds University, England, is now in this country taking a post graduate course at Columbia University.

Dr. Hermann Schneider, Dean of the College of Engineering and Commerce, University of Cincinnati, was on the program to address the meeting on Industrial Education, but unfortunately Dean Schneider was prevented by illness from attending.

While it is a source of gratification to the chemist to witness the great improvement in his status in the tanning industry, it must be recognized that the tanner is transferring a part of the burden which he has himself carried so long. It is not enough to offer the tanner explanations of his processes full of high sounding phrases. Upon the close co-operation of the tanner and the chemist will depend the progress in our industry in the future. The objective is to produce a better product at a lower cost and the responsibility is mutual for the one cannot accomplish the greatest good without full co-operation from the other. It is

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now squarely up to the chemist to justify the confidence which is being reposed in him to a constantly increasing degree and to realize the great expectations of the leaders of the tanning industry.

THE OFFICIAL METHOD OF TANNIN ANALYSIS— SOME OBSERVATIONS AND SUGGESTIONS

By H. C. Reed and T. Blackadder

Rec'd. Oct. 27, 1921

In the recent past the official method of tannin analysis has been subjected to considerable criticism. It is the writers' opinion that a good deal of this criticism is based upon a misconception of what an analysis by this method represents. At the time our official method was first made official the point in mind was to have a measure of the monetary value of vegetable tanning materials. This called for the observation of two points. The first and more important point of the two was that the method could be followed in routine laboratories and be capable under such conditions of producing concordant results; the second point was that the method should as nearly as possible give a measure of that portion of the tanning material which was of use to the tanner in converting his hide into leather.

There has never been any claim made that the method gave a measure of the chemical constituents of a tanning material and we believe that criticism is in some part directed at the present method owing to a misunderstanding on this point. There is obviously a considerable difference in the tanning value of a vegetable tanning material and the tannin value. The tanning value would appear measurable in terms of the amount of matter which is removed from the material and put into the leather during the process of tannage; whereas the tannin value would be entirely dependent on the definition which we adopted for tannin. At the present day it seems previous to say that we can adopt a strict definition of what is tannin and, therefore, it seems that we must progress along the line of a constructive criticism of our present method rather than by destroying what we have by adopting a new definition of tannin which might at any future

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time have to be discarded in the light of further advance of our knowledge.

It seems that in order to arrive at a practical definition of what we are attempting to measure, our best standard would be the tannery itself, in other words, our method should give as its results for tanning matter a measure which is comparable with the amount of matter which the tanner can put into his leather in actual tanning operation. It does not seem right for instance to adopt as a standard the amount of material which can be fixed by hide powder so that it will withstand immediate washing with water and claim that this is a true measure, for not only is this unlike the tannery operation, but we have not yet sufficient knowledge to assert that materials which will make leather out of hide are fixed in a short period of time so as to withstand immediate washing in water.

Thus to have a method which is to be of use not only as a medium for fixing the monetary value of our tanning materials, but also to form a guide to the tanner as to what results he might expect in terms of leather from a given tanning material it is necessary that the method should as far as possible parellel the conditions under which that material is to be used. The possibility of strict parallelism is obviously absurd and it is therefore necessary for the chemist to devise a set of conditions in the laboratory which will enable him within a reasonable length of time to obtain a measure of what we might call the tanning value of these materials which will as closely as possible compare with the measure which would be obtained by a method strictly paralleling average yard conditions. It would further appear that the real test of the value of the method will come from actual experience of the average tanner who by observation over an extended period of time is able to judge whether or not he is obtaining in his leather the full measure of tanning material which his analysis would lead him to expect. It would appear up to the present time that the present method has given the tanner of heavy leather a pretty good estimate of the amount of material he could transfer from his vegetable tanning materials into his leather.

If it were not from the fact that the recent advances in the theoretical and practical fields seem to demonstrate the possi-

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bility and necessity of improvement in the present method the authors would hesitate to recommend any change in it as it must be borne in mind when considering any changes that the present method has proven a very satisfactory standard for selling and buying vegetable tanning materials.

If we adopt as our basis of consideration the two points mentioned above: namely, the concordancy of results, and the obtaining of a practical measure of the tanning value of the materials in question, it appears that there are two questions at least on which we can effect improvements; these might be stated as the question of determining the insolubles and the question of non-tan absorption. This latter carries with it another question to be considered,—namely, the acidity of the hide powder and of the solution during detannization. The consensus of opinion appears to uphold the view that in determining the insolubles according to the present method we are penalizing certain materials which are high in phlobaphenes and when we look into the theory of this matter this opinion is upheld in the light of recent work, noticeably that of Schultz.[1]

It would seem that a vegetable tannin when dissolved in water can exist in three states: a portion may exist in the most finely divided form in true solution;[2] the major portion probably exists in less finely dispersed form as a colloid, and this we term a colloid solution; and the third part may exist in still less finely dispersed condition and as this third part can be filtered out, we would term it a suspension and in our present method of analysis this suspension would be called insoluble matter. Now according to experience in all chemical fields we have no other possibility before us than to believe that these three states, or modifications of tannin in solution, are striving to pass each into the other con-

[1] G. W. Schultz, This JOUR., 16, 349, 1921.

[2] It is noteworthy that when the tannin molecule is in this simple form it appears not to form a precipitate with gelatin and would probably therefore not tan hide. It would of course be possible for it, in presence of hide, to associate to the intermediate size molecule of colloid dimensions and tan hide as fast as this association went forward. But this would probably take time. Further, it is interesting to remember that in all physical changes of state it is a general rule that the unstable form is first formed, this then changing to the stable form. Thus in the case of dissolving the insolubles by addition of water the probable first step would be the formation of simple tannin molecules which would then reassociate to form the colloid molecules. This is important in its bearing on the Wilson-Kern method of analysis where the hide powder after tanning is washed with a large volume of water. It appears very possible that material which would truly be classed as leather forming, or tannin, from the tanners view point, is washed out in this simple molecule form and does not respond to a gelatine test. (Schultz, *loc cit.*)

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tinuously. Also after sufficient length of time, under any given conditions such as exist in a solution of analytical strength held at a prescribed temperature, an equilibrium will finally be reached. At the time when this equilibrium is reached we must not think that change from one state into another has ceased. What really is happening is that equal amounts of colloid and the insolubles are being exchanged between these two states continuously, and in fact between each pair of the three states, so that the total amount of each state remains constant. Now of these three states it appears highly probable that the colloid state alone is capable of tanning quickly and possibly the only one which is capable of tanning directly when a piece of hide is immersed in this solution. Thus when detannizing with hide powder we are removing the colloid part of the solution which immediately upsets the state of equilibrium which was existing. We have at once a disintegration of the large particles or insolubles into the middle size particles or the colloid at a speed faster than the now remaining smaller amount of colloid is associating to form the large particles. The net result is that the amount of insolubles is decreasing and we are forming colloid which very rapidly combines with the hide and we appear to be tanning with the insoluble matter. A similar result is of course obtained from the small amount which is in true solution, but this amount is probably extremely small and plays a much less important part in the reaction. There are many practical experiences which bear out our theory in this matter and for the present it appears that we may safely adopt this theory in considering the point in question. Turning to the practical side of the matter is it not a fact that a careful tanner makes a point of utilizing as far as he can the insoluble part of his tanning materials, having realized from experience that they do possess a tanning value? At the same time, all of our insolubles are not valuable as a tanning material for undoubtedly some non-tans associate similarly to large particles forming insolubles, and there is extraneous matter, which possibly ought not to be there, present in our insolubles also. We believe however that our method of analysis should take cognizance of such portion of the insoluble matter as is capable of entering into combination with the hide.

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Suggestions have been made to hold these insoluble matters in solution by such means as raising the temperature of the analysis solution or by the addition of other solvents, but these methods are to be deprecated for the reason that they will act on the insoluble non-tan matter as well as on the insoluble tanning matter. From practical experiments in the authors' laboratory it appears feasible and advisable to effect an improvement in the insoluble determination by paralleling the tanning process. In other words, it appears feasible to shake the analysis solution with hide removing both colloid and such portion of the insoluble matter as will go into the colloid state, and have tanning value in this state, and determine the insoluble matter in this detannized solution. Further work is anticipated along this line.

At the same time that we consider the value of these insoluble matters, we must consider their disadvantage. We must consider that they are also a potential source of loss and it would seem that a measure of the solubility of the tanning material, more especially when this is an extract, should be included in our analysis. We believe that this solubility should be measured at a considerably higher concentration than is used in the present method of analysis. Possibly a concentration more comparable with the strength of the liquor normally made with extracts would give the most valuable information to the tanner on this question of solubility.

When we come to consider the second question,—namely, the absorption of non-tans, we have not a complete enough knowledge of the facts of the case, for chemical theory to give us much help. We are forced to rely almost entirely for guidance to the finger-post which reads,—"parallel your tannery conditions."

The question of how much non-tan absorption does occur will always be open to question as long as we are without a definition of what we are to call tannin, but it does seem to be a fact that certain things which we cannot conceive of ever being included in a definition of tannin, such as salts and possibly organic matters similar to gallic acid would fall in this class. We know that such matters are absorbed, in the manner which we need not discuss at present, by hide powder and it would also seem an axiom that the greater the amount of hide powder the greater the

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absorption will be. Now the tanner uses considerably less hide per unit of tanning matter than we use in our present official method and we are thus led on to question the necessity of our using the quantity we are to-day. If this amount can be reduced we should expect to reduce any errors due to non-tan absorption. At the same time, if, when we are carrying out our experiments to determine whether this amount can be reduced and as to how much it can be reduced, we bear in mind this expectation, these experiments may give us valuable information as to the actual amount of non-tans which are being absorbed with the various amounts of hide powder. At the same time as these experiments are being carried out we must also bear in mind two other factors:—namely, the effect of the pretannage with other materials than chromium sulphate as it is used to-day, and the effect of varying the acidity which in our present day solution is considerably less than the acidity of the tanning liquor when used in the tannery.

The writers have sought an answer to the question of the effect of reducing the amount of hide powder by what seemed the only possible method,—namely, making the attempt. It appears from the work which has so far been carried out that it is possible to reduce the amount of hide powder and to use other pretanning materials, such as quinone, always bearing in mind the paralleling of tannery conditions and to obtain what appears to them to be a fair estimate of the amount of tanning matter in the tanning material under examination. It is also noteworthy that they are led to believe that the amount of non-tan absorption in the present method of analysis is very considerably less than one might be led to expect when considering the amount of criticism which has been directed at this point.

The question of the acidity of the solution at the time of detannization has long been recognized as being of fundamental importance, but the advent of synthetic tanning materials has made this point of much greater importance than heretofore. These materials are of course of entirely different acidity from our vegetable tanning materials and in the ordinary run of analyses the conditions at the time of detannization are entirely different in the case of a synthetic material from what they are

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in the case of a vegetable material. It is also easily demonstrated how the apparent tanning value of these synthetic materials is influenced by the acidity at the time of detannization. It would appear to be very necessary to standardize this condition of acidity at the time of detannization and this point appears worthy of considerable research in the hands of a highly trained chemist. It must also be remembered that in all work relating to the acidity of solutions in contact with hide powder that the present extent of our knowledge of this material appears to show that it is not directly comparable with gelatine and that we would be very liable to be led into error should we attempt to transfer knowledge derived from past experiments with gelatine to a problem where the material used is hide powder.

CONTRIBUTION FROM THE REED LABORATORIES.

THE WARBLE FLY PROBLEM[1]

By Alfred Seymour-Jones

The warble fly problem has for many years past forced itself into prominence because of the serious financial losses accruing to stockraiser, dairyman, butcher, and tanner. The stockraiser's cattle fail to fatten, the dairyman loses milk, the butcher suffers loss through "blown beef," and the tanner finds the hides deteriorated by trumpet shaped holes down the spinal area. The total monetary loss resulting from the ravages of the warble fly cannot be accurately estimated, nevertheless it must amount to a very large figure. But that is to put the situation on a low plane. Let us approach the problem from the higher and nobler aspect, namely the untold suffering and agony caused to the patient, long-suffering, dumb animals, arising from the numerous "boils" festering in an area beyond the reach of their mouths or limbs. Job with all his affliction of boils was never as patient as the cattle tormented with warble bots.

Finally a point of human interest must not be lost sight of. Hides having warble holes are tanned for shoe leather soles, the holes being frequently cleverly hidden. There is a certain amount

[1]Presented to the Division of Leather Chemistry at the 62nd meeting of the American Chemical Society, New York City, September 6 to 10, 1921. Published by courtesy of the American Chemical Society.

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of evidence to prove that individuals wearing such soled shoes have contracted colds and even death as a result of getting wet feet. With such an indictment of the warble fly, a strong case has been made out to justify the expenditure of public funds on research in the interests of cattle and humanity.

The greater part of the life cycle of the warble fly has been well known for more than a hundred years, thanks to the work of Bracy Clark early last century. Much however remained to be discovered as to the method of egg laying by the fly and of the newly hatched larva's entrance into the bodies of the cattle. Now through the investigations and observations of an entomologist, Professor George H. Carpenter, of the Royal College of Science, Dublin, and two veterinary surgeons, Dr. Seymour Hadwen, Dominion of Canada Pathologist, Health of Animals Branch, and Dr. Glaeser of Berlin, Germany, who independently published the results of their researches in 1914, we are in possession of nearly the whole of the warble fly's life cycle. Dr. Carpenter summarises his results in the following words:—

"The large, somewhat barrel-shaped maggots that are found in cattle in swellings or "warbles" just beneath the skin of the back for a breadth of several inches along either side of the spine, are well known to all stock farmers. At the summit of each warble is a small round hole bored through the skin so as to allow fresh air to reach the breathing-openings at the tail-end of the maggot, which is turned upwards. The cavity in which the maggot lies becomes filled with half-liquid products of inflammation; on these the parasitic insect feeds. When maggots are numerous in a beast, there is resulting weakness and loss of condition, and the holes that pierce the skin greatly reduce the value of the hide for tanning purposes. It is not easy to estimate the loss caused the nation through these parasites, but reliable computations suggest that some millions of pounds a year would be added to the value of our livestock if warble maggots were exterminated.

"In these "ripe" maggots in the cattle's backs we see the best known stage of a remarkable and fascinating insect life-history. They are to be observed thus during four or five months in fair abundance from February to May inclusive, but in smaller num-

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bers they may be noticed as early as December and as late as June or even July. Close examination shows that there are two kinds of these maggots; a smaller, more spiny sort, called *Hypoderma lineatum,* ripens earlier than a larger kind with the spines fewer and weaker, known as *Hypoderma bovis.* The name *Hypoderma* signifies that the parasite lives ***beneath the skin.*** By means of the spines, which are arranged in rows across the segments of the body, the maggot is able to fix itself in preparation for movement. At the end of the body farthest away from the breathing hole is the mouth, which is provided with small hooks, but the soft broken-up tissue on which it feeds requires but little biting. In all essential points of structure the warble-maggot is like the maggot of the blue-bottle fly, but in the "ripe" condition it is relatively stouter and rounded at both ends.

"When the maggot has become fully grown it works its way out of the beast's skin, through the breathing hole, and falls to the ground. Then it makes its way to some convenient shelter and undergoes a great change. Its firm outer coat (cuticle) separates from the living tissue beneath and becomes hard and dense, so as to form a *puparium* or protective case for the *pupa* or resting-stage of the insect's life-history, which is gradually built up inside. After an interval of six weeks—more or less—according to the weather conditions—a roundish lid splits off from the head-end of the puparium, and the fly, the adult insect, comes out.

"Warble flies are hairy insects, somewhat resembling small humble-bees. There are two distinct kinds, corresponding to the two kinds of maggot mentioned above. *Hypoderma bovis,* is the larger warble fly, with the front region of the body hairy, and the tail hairs lemon-yellow in color. *Hypoderma lineatum* is smaller, with the front part of the body smooth and shiny, with alternative dark and pale lines running lengthwise (hence the *lineatum* or 'lined') and with the tail hairs bright foxy-red. These flies have no jaws for biting, and they do not appear to take any food. They can not in any way pierce or sting the cattle, yet when they approach grazing animals, the latter show great alarm, jump and leap, and rush about the fields with their tails in the air. Because these flies cause 'gadding' in cattle they used to be called gad-flies, and this name is now often applied to the bloodsucking breeze-flies (Tabanids), which frequently bite cattle in order

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to feed on their blood. The breeze-fly grubs live in damp earth devouring worms and slugs; breeze-flies, therefore, have nothing to do with warble flies, though often confused with them. Of the two kinds of warble flies, *H. lineatum* is the earlier, appearing on the wing in May and June, whereas *H. bovis* is seen principally in July and August. They fly in warm sunshine with a distinct though not very often loud hum, and their object in approaching the cattle is to lay their eggs on the beast's hairs. Why this action should be so terrifying to the cattle is a mystery, but the excitement and violent exercise, induced by the insects, on hot days, results in loss of condition and lessening of the supply of meat and milk.

"Both kinds of warble fly lay their eggs mostly on the legs of the cattle. It appears that they very rarely lay on the back, and the practice of dressing beasts' backs with oil and tar in summer time to keep the flies away has been proved useless by a series of experiments carried through several years. A warble fly's egg is about $^1/_{20}$ inch long, narrowly oval in shape, with a grooved flange-like process at one end; the groove fits beautifully over the beast's hair, to which the egg is fastened. Many people still believe that the fly pierces the ox's skin and lays the egg underneath, but this view was shown many years ago to be incorrect. There is a curious difference in the egg-laying habits of the two kinds of warble fly. *Hypoderma bovis* lays every egg by itself close to the base of a hair, while *Hypoderma lineatum* lays a number of eggs in a row along a single hair. If cattle have access to shade or water, they can obtain considerable protection from the flies, as the flies are not usually active except in sunshine, and when the cattle are standing in a pond, the legs on which the eggs are laid, are mostly under water.

"About four days after laying the warble fly's egg is hatched, the tiny first-stage maggot breaking its way out through the upper hole, where a crack in the hatched egg-shell is conspicuous. This *first stage maggot* is about $^1/_{30}$ inch long, with sharp mouth-hooks and spines, very large and strong in proportion to the maggot's size. It crawls down the hair, and in the course of a few hours burrows into the beast's skin and disappears. The entrance of the newly-hatched warble maggot into the ox's body in the manner

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denoted has been observed by Prof. Carpenter and his colleagues in Ireland, and by Dr. Seymour Hadwen in Canada. All through the late spring and summer, from early May to September, multitudes of tiny maggots are thus boring into the bodies of cattle.

"What exactly becomes of them after their entrance is not known, but it is certain that in some way they reach the gullet where the *second-stage maggots* may be found in numbers from September till February, embedded in the loose fibrous tissue of the gullet-wall. In this stage the maggot is elongate and nearly cylindrical, the mouth-hooks being feeble, the cuticle smooth, and the spines excessively minute, except a few black ones at the tail-end near the breathing-holes. These maggots, when first discovered in the gullet-wall, were believed to afford evidence that entrance must have been gained through the beast, on which eggs had been laid, having licked the eggs or young maggots into its mouth. This opinion has been disproved by means of an extensive series of experiments with muzzled calves. In the final form of these trials, a number of calves with leather muzzles covered with wire cages so that licking was impossible, were allowed to roam during the summer about a field in company with many calves grazing as usual. At night, and at feeding time, when the muzzles were taken off, the calves necks were tied between stakes so that licking was still impossible. In the count of warble maggots the next year it was found that the muzzled calves had a somewhat higher average than their untreated companions. Hence we have the confirmation of the conclusion reached by direct observations mentioned above, that the newly-hatched maggot gains access to the body by boring through the skin and not being licked into the mouth.

"From the gullet the maggots, still in the second stage, make their way through the muscles of the body-wall and between the sections of the back-bone to the positions in the back where we find them from November onwards. Hence they become changed into the *third-stage,* in which the rows of spines are well developed and quite distinct. The maggot in this stage bores a hole through the beast's skin, ensuring itself a supply of air, and a way of escape when the maggot life shall be over. In due time the third-stage is succeeded by the *fourth-stage,* which when it becomes "ripe," is ready to leave the host-animal's body."

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The warble fly problem has naturally attracted much attention in the United States and the work of Curtice and Riley is known to all students of the subject. Twenty years ago they observed that in North America the female *Hypoderma lineatum* lays her eggs mostly on the heels, and they concluded that, as in the case of the horse bot-fly (*Gastrophilus equi*), the newly hatched maggots must be licked in by the cattle. Then it was believed that they bored through the mucous coat of the gullet, and, after resting awhile in its sub-mucous coat, worked their way to the final position beneath the skin of the back.

In order to ascertain if possible the exact method of the maggot's entrance, experiments were carried out for ten years at the Irish Department of Agriculture Station, Ballyhaise, County Cavan, by Dr. Carpenter and his co-workers. Those experiments on muzzling calves have already been referred to and were most conclusive. In addition, Dr. Carpenter carried out experiments on calves such as protection against attacks in the region of the back and against attacks of the fly on the legs by clothing the calves in trousers. All the results confirmed the opinion that the entrance of the maggot was by other means, and not by licking in.

After enumerating experiments and observations, Dr. Carpenter and the late Mr. Thomas R. Hewitt state in their brochure "(Some New Observations on the Life History of the Warble Flies," 1914) :—"Besides the experiments at Ballyhaise, a number of observations on warble flies and maggots have been carried on at Athenry Agricultural Station by our colleague, Mr. James Duncan, B. Sc., who has received much valuable help from Mr. R. Y. Smith, the farm manager, and Mr. Lang, the cattle-herd. At Athenry *Hypoderma lineatum* appears to be the common species, whereas at Ballyhaise, *H. bovis* is the more abundant; and it is well known that the latter species appears later in the summer than the former. In the first week of June Mr. Duncan told us that the eggs of *H. lineatum* were plentiful on cows at Athenry, on the hairs of the thighs not far below the root of the tail, and that a few days after the eggs had been laid Messrs. Smith and Lang observed a soreness in the neighboring region of the skin with a discharge of matter. One of us (G. H. C.)

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accordingly went to Athenry accompanied by Mr. T. K. Reddin, who is associated with us in this inquiry. The region of the body where these eggs were laid was very convenient for examination, and the milch cows, standing quietly in the byre, were better subjects for observation than restless calves in the field. We found that the cow's skin near the newly-hatched eggs was perforated by minute holes from which flowed a watery discharge which hardened on the surface to a scaly deposit, and that after a day or two the region affected became covered with small pimples; these disappeared a few days later. On squeezing the skin of the earliest 'case' that could be obtained, some clear, watery fluid exuded, and a smear of this examined microscopically was found to contain a newly-hatched maggot of *Hypoderma lineatum*.

"This satisfactory observation incited to further work at the problem later in the summer with *H. bovis* at Ballyhaise, where one of us (T. R. H.) has been in charge of the experiments during the past two seasons. In July twenty-four maggots were hatched in the incubator, and some of them were used for observations as to the behavior when placed on a calf's body. Glaeser, in 1913, had tried to carry out observations of this kind, by placing maggots on a shaved portion of a calf's skin; he found that they made no effort to bore through. Instead of being shaved, a small patch on the shoulder of one of the Ballyhaise calves was clipped, so as to have the conditions as normal as possible, and newly-hatched maggots of *H. bovis* were placed on it. Immediately they started crawling down the clipped hairs to the skin, and, as soon as they reached the surface, they began to burrow. On account of their small size it is hard to discern them, but by careful watching through a lens it was seen that they enter perpendicularly to the surface, evidently cutting into the epidermis with their mouth-hooks and occasionally bending their bodies. Mr. R. G. Whelan, Superintendent of the Ballyhaise Agricultural Station, kindly helped in the observations and confirmed them. Six hours after having been placed on the calf, the maggots disappeared completely. Next morning the spots where they had entered were marked with little pimples, like those on the Athenry animals, easily to be seen with the naked eye. These increased slightly in size, but soon healed up, and in less than a week not

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a trace of the maggots' entrance could be found. The boring in of the maggots seemed at first to cause the calf a little pain, but the symptoms of discomfort soon passed away."

The accuracy of these observations can leave us in no doubt as to the final settlement of the long disputed point in the life history of the warble flies.

The question has frequently been asked, why does the warble fly show a preference for the hairs of the cattle's heel or hind quarters? It has been suggested, with some justification, that primarily the fly is attracted by the aroma peculiar to cattle, and to the heel hairs especially because between and at the apex of each hoof bifurcation is a gland yielding a strong smelling oil. Failing to lay their eggs on the heel hairs, they choose a spot as near to as possible.

The newly hatched larva possesses a powerful boring scheme. When the larva has emerged from its shell, it descends the hair; meeting the obstructing skin, it would appear to grip the skin with the two mouth hooks, and, using the hair as a pushing post and the pit or follicle from which the hair grows as a means of ingress (as Dr. Hadwen has shown), it commences to dig a hole into and through the skin with the spade-like median tooth. The *H. bovis* being single egg layers on single hairs, each larva has to dig its own entrance to the body, but *H. lineatum* lay eggs in rows, and their larvae would appear to follow each other through the hole made by the first larva, and in doing so the hole slightly enlarges. The increased irritation causes an increased discharge of inflammation substance.

The peregrinations of the first stage larvae through the cattle's anatomy remains a mystery. Of the large number of larvae which find entrance, a very large proportion fail to reach the second and third stages. The migrations of the second stage larvae from the gullet to the back have been traced by the Dutch Veterinarian, Dr. Koorevaar, and other European investigators.

Dr. Seymour Hadwen has made some interesting experiments with second stage maggots dissected out of a cow's gullet, which he inserted under the skin on a calf's back. The calf was killed a few weeks later. A gelatinous patch was found at the point where the larvae had been introduced. This gelatinous track

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could be followed because "no special care was taken in removing the larvae from the gullet; hence these became contaminated with bacteria and naturally carried infection wherever they went, thus leaving a plain trail." These experiments were carried out with well developed second stage larvae, consequently were likely to survive in any experiment. Dr. Seymour Hadwen arrived at the following conclusions:—(a) The larvae are found in the submucosa of the oesophagus and gradually work their way towards the diaphramatic end of the oesophagus. (b) They may follow the posterior borders of the ribs under the pleura. (c) They may enter the neural canal. (d) Evidences that the posterior foramen is the means of ingress and exit has been noted. (e) Finally the larvae follow the connective tissue closely.

Why the third stage larvae are found on the living cattle to form lumps only in the region of the spine is an interesting point. Certain reasons suggest themselves. (1) The spinal area cannot be reached by the animal with its mouth or feet. (2) It is the only quiet area of skin and cannot be lain on or the emerging maggots crushed. But it is questionable whether those reasons are sound. Every tanner has observed, after the hides have been swollen in the lime liquors, that there are many more warble bots on the flesh-side of the hide than are accounted for by the bot lumps, and they may cover a wider area than that associated with the spine. If these warble bot sites outside the spinal area are closely examined they will be found under-developed, and the evidence of nibbling the hide is absent. This phase has interested me and from numerous observations made I conclude that the barrier found by the larvae is that formed by the *panniculus carnosus* (red muscle). This is a powerful muscle of the smooth involuntary type, which enables the animal to twitch the skin when bitten by a fly. Its distribution varies in all cattle. In some it is strong, covering large areas, in others thin and weak, in others again it forms a compact sheet with few interstices or separations. It may be more or less non-existent or heavily separated. If sections are made of the skin where the larvae has raised the well known lump and is ready to emerge, it will be seen that the red muscle is non-existent, and, where the larva has failed to burrow through, the red muscle is thick.

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The largest number of warble bots are found in young calves and yearlings. Here the red muscle is young, thin, and heavily separated. As the beast ages, less and less warble bots emerge, and the red muscle becomes tougher, thicker, and less separated.

The two species of warble flies normally confine their attentions to the bovine species, just as *H. diana* confines its attentions to deer, but maggots of *H. bovis* are not infrequently found beneath the skin of horses.

The English Ministry of Agriculture in collaboration with the Scottish Board and the Department of Agriculture for Ireland has formed a commission of experts to investigate methods for exterminating these two pests. Their labors are as yet unfinished, but it will be of interest to give some idea of their work.

The ideal method, upon which we are all agreed, for exterminating the plague is to squeeze out the bots from the animal's back as they reach maturity and destroy them. This method has been extensively recommended in all countries where the fly is troublesome. The Irish Department of Agriculture, under Dr. Carpenter, commenced such experiments in 1904 on the farm at Ballyhaise, County Cavan. For several successive years a count of the maggots was made each spring and it was found that their numbers became much reduced. In 1914 it was decided to attempt the extermination of the insects in the cattle of an isolated area and Clare Island, at the mouth of Clew Bay, County Mayo, Ireland, three miles from the nearest point of the mainland, was selected for this experiment. In spite of its isolation from the mainland many difficulties were experienced, not least the reluctance of some of the farmers to co-operate in the test. The result of the experiment may be summed up by giving the figures. In 1915, 6,172 warble bots were squeezed out; 1916, 4,349; 1917, 3,571; 1918, 2,027; 1919, 633; and in 1920 the Island was free from warbles.

Dr. Carpenter sums up the results as follows:—"The general conclusions to be drawn from this piece of work are that the insects can be exterminated on an isolated area by persevering effort continued for a period of seven months each year through a sufficient number of years. Probably with a start in January and in a district less difficult than Clare Island, success might be attained after two years' work.

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The Warble Committee considered several lines of experiment for exterminating the warble pest; preventing the fly striking to lay its eggs, to kill the bots by hypodermic injections, and to kill them by some external application before they emerge.

The first scheme has been frequently tried in past years but no proof of the efficacy of dressing for this purpose has been given. In the opinion of some it might be considered dangerous on account of the grave probability of the fly, finding it could not deposit its eggs, changing its mode of life or habits; consequently the pest might become greater than ever. Nevertheless one experiment was tried. A mixture of bird lime material was mixed with a small quantity of birch tar oil, the well known scent in Russian leather. This mixture was anointed on the hind quarters of a few cattle. It was expected that the smell of the birch tar oil would repel the fly, and if she penetrated to the hairs then the bird lime would prevent her laying her eggs. This scheme had to be abandoned on account of the tails of the cattle adhering to the tacky material, causing the animals to stampede. Also there was the probability of the fly changing her habits rather than be defeated in laying her eggs.

In view of this, the committee turned their attention to the safer method of killing the warble bots in the backs of the cattle by means of dressings. Among the many chemical substances tested may be mentioned, McDougall's Fly Oil; Eblana Fluid; Liver of sulphur paste; sulphur paste; turpentine and Archangel tar; liver of sulphur, tar and turpentine; linseed oil; sheep dip (arsenic); sulphur, spirits of tar and train oil; linseed oil and carbon disulphide; mustard and vaseline; tobacco powder (dry); tobacco paste; tobacco powder and carbolic acid; tobacco powder in varying solution strengths. The most encouraging results were obtained from a mixture of tobacco powder steeped in water and mixed with lime. This was made as follows:—Take three or four pounds of tobacco powder and steep for twenty-four hours in one gallon of water to which two to four pounds of quick lime has been previously added; strain through a course muslin cloth. This wash is applied when the maggots are nearly ready to emerge, and it may be advantageous if a second dressing be given, by means of a cloth over the area, two days after the first. The ex-

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perimental results on a number of cattle on different farms have given from 80 to 96 per cent of kills. Much of the success depends on the operator fairly and squarely applying the mixture, but when done efficiently there is reason to hope that the fly might be exterminated inside three years within an area where all the cattle are thus treated.

The other substances tried were abandoned for various reasons, some through failure to kill the bots in sufficient numbers, and some due to their injuring the animal's skin.

The hypodermic injections were negative in their results.

The labors of the British Warble Fly Commission have not yet been completed but I have given sufficient information to show that there are safe and practical methods for the eradication of these two warble flies, which can be applied by any stockraiser. The work of such a commission must of necessity be slow on account of the operation of the flies being annual, but being doggedly pursued, by experts, we have every reason to expect that our final results will be welcomed throughout the world.

I cannot conclude without recording a tribute to the Irish Department of Agriculture for their generous help and for placing several farm stocks at our disposal, and more particularly to Professor George H. Carpenter, for the persistent manner in which he has striven to complete our knowledge of the life history of the warble fly and to devise means to circumvent its life on farms.

In the interests of the invaluable, long-suffering, dumb animals I appeal to my American colleagues to assist in the noble work of exterminating both *Hypoderma bovis* and *Hypoderma lineatum* from our respective countries ,and so bring happiness with freedom from suffering from this pest to cattle.

Wrexham, N. Wales.

THE EFFECT OF HARD WATER UPON TANNIN

By H. C. Reed

Rec'd. Oct. 31. 1921

The committee of the Association appointed for the purpose of determining the effect of hard water upon tannin, abandoned the investigation without arriving at any definite conclusion. It is

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generally admitted that hard water has an untoward effect in tanning and practical tanners, who have had experience, are ready to bear witness to this fact. As a matter then of no mean importance to the leather industry, it seems most unfortunate that the work of the committee should be discontinued, particularly so in view of the cause as expressed in the chairman's final report.[1] The reason there given is to the effect that conclusions to be drawn from the data obtained from the committee work of 1917 and 1918 had best be deferred to such time as a theory of tannage had been conclusively established. The indefinite postponement appears to be due primarily to the result of certain investigations made by Wilson and Kern which the chairman of the committee cites. He says that the results of the Wilson and Kern work definitely proved that solutions of calcium sulphate analyzed by the hide powder method actually showed a percentage of tannin. An error was evidently made in this interpretation, as a reference to the article referred to[2] discloses that the author's claim is that calcium sulphate, analyzed by the hide powder method, will give a non-tannin in excess of 100 per cent, and therefore a minus tannin figure. What is of moment, however, is that the investigation referred to had a decided influence in effecting the early demise of the committee work.

From the article[3] we find the conclusion is drawn that the official method for tannin estimation is unsuited for the purpose of determining the effect of hard water upon tannin since, under certain conditions it will give erroneous non-tannin returns. In the case of hard waters, the error in the non-tannin item is attributed to the fact that results in excess of 100 per cent will be obtained when analyzing pure solutions of the salts that produce hard waters. The author states that the high non-tannins found are "due to the erroneous assumption in the hide powder method that the concentration of solute in the solution absorbed by the hide powder is the same as in the solution surrounding the hide fibers." In order to prove the contention the author carried out certain tests which he contends substantiate his claim, and since the evidence submitted had so great an influence with the

[1] This Jour., 1919, p. 505.
[2] This Jour., 1919, p. 93.
[3] *loc cit.*

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committee, it may be of interest to inquire whether sufficient proof was offered to warrant the winding up of the investigation.

Referring then to the experimental data[4] we find that a 0.05 per cent solution of calcium sulphate, analyzed by the hide powder method, gave a determination of 117 per cent non-tannin. A 0.05 per cent calcium sulphate solution was used to dilute 11.30 grams of quebracho extract to a litre for analysis and for comparison a second portion of like amount was diluted with distilled water to a litre. The author states that the results to be expected can be calculated; the presence of the calcium sulphate will increase the soluble matter by 0.5 grams per litre but will increase the non-tannin matter by $1.17 \times 0.5 = 0.585$ grams per litre, if we may assume that the tannin is without action upon the salt and does not influence the distribution of salt between the solution absorbed by and that surrounding the hide fibers. The error is figured as 0.75 per cent less tannin when calcium sulphate water is the solvent than when distilled water is the solvent, owing entirely to the increase in the non-tannin item from the unequal distribution of the salt solution referred to. The actual results of the analyses are then submitted as follows:

	Diluted with distilled water	Diluted with calcium sulphate water
Total solids	48.34	52.44
Soluble matter	47.23	49.94
Insolubles	1.11	2.50
Non-tannins	11.00	14.42
Tannin	36.23	35.52

$$36.23 - 35.52 = 0.71$$

The actual loss in tannin is 0.71 per cent and the loss expected from the increase in non-tannin 0.75 per cent by calculation.

Employing the method of calculation given by the author, which he shows to be dependent upon the results of the analysis of a pure water solution of calcium sulphate by the hide powder method, we can figure the analysis to be expected. This is as follows:

	Calcium sulphate calculated
Total solids	52.76
Soluble matter	51.65
Insolubles	1.11
Non-tannins	16.17
Tannin	35.48

$$36.23 - 35.48 = 0.75$$

[4] This Jour, 1919, p. 97.

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Therefore, according to the author, the actual analysis of the quebracho extract diluted with calcium sulphate water should show a non-tannin of 16.17 per cent, whereas the actual non-tannin obtained amounted to but 14.42 per cent, a difference of 1.75 per cent.

The article then says, "we might now be inclined to believe that calcium sulphate does not cause any appreciable loss of tannin..... ....." In other words, since the tannin loss shown by analysis is 0.71 per cent, and the expected loss by calculation 0.75 per cent, the author's theory and experimental data are confirmed. But it appears as though the increase in the non-tannins should have been from 11.00 per cent by distilled water analysis to 16.17 per cent by calcium sulphate water analysis, or an actual increase of 5.17 per cent instead of from 11.00 per cent to 14.42 per cent, an actual increase of only 3.42 per cent.

Let us assume that the presence of calcium sulphate produced no effect whatever upon the non-tannin figure and calculate what the analysis would be under such an assumption. The result would be as follows:

	Calcium sulphate No effect upon analysis
Total solids	52.76
Soluble matter	51.65
Insolubles	1.11
Non-tannins	15.42
Tannin	36.23

Thus we find that if the presence of calcium sulphate in the water used for solution had no effect upon the non-tannin this figure would have been 15.42 per cent, which is higher by exactly 1.00 per cent than actually obtained by analysis. Not only do the author's figures prove that there is no loss of tannin by increase of non-tannin but that there must be a gain in tannin from a decrease in non-tannins. What the results of the analyses show is a loss in tannin by increase in insolubles, and this is an actual loss indicated by the hide powder method, and by no manner of means an immaterial loss. The analyses might raise yet another question; whether it is safe to assume from the results obtained in non- tannins by analysis of pure water solutions of salts that corresponding results will be obtained when salts are in solution with tannins. The concentrations of a salt solution within and

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exterior to hide powder may be quite unlike the concentrations of a salt solution within and exterior to partly tanned hide powder.

It might be claimed that the calcium sulphate that did not take part in increasing non-tannins was utilized in precipitation of tannin, as shown by the increase of insolubles from 1.11 per cent in the case of distilled water to 2.50 per cent with calcium sulphate water a total increase of 1.39 per cent. It is, however, a well recognized fact that in a tannin precipitate of this character the tannin weight is many times that of the precipitating agent, so that the amount of calcium consumed in the 1.39 per cent excess insoulbles must necessarily be of little consequence. Moreover, it is quite possible that the calcium tannate precipitate is split up in agitating the solution with hide powder, the tannin being absorbed and the base appearing as non-tannin.

In commenting upon certain differences in results shown by members participating in the work of the committee on the effect of hard water tannin the suggestion is advanced[5] that since "both lime and sulphuric acid combine with hide substance it seems likely that an appreciable amount of calcium sulphate would combine with the hide, especially since both ions of this salt are divalent." If both ions of calcium sulphate combine with hide it is difficult to see how the concentration of solute in the solution absorbed can be less than the concentration of the solution surrounding the hide fibers.

Now a word as to use of the hide powder method in determining the effect of hard water upon tannin. The writer is not bigoted to the degree that he sees in the official method of tannin analysis a means of solving all the problems that confront the leather chemist. There are limitations in all things, methods of analysis included; but there are also safe and sane ways of employing methods of analysis. Also it is conceivable that erroneous conclusions may be drawn in interpreting results given by a perfectly reliable method. On the assumption that certain predictions. must be verified a method may be blamed for not confirming the predictions. It would appear as though the question as to the loss of tannin from the use of hard water is more properly a matter of individual research than of committee work. The

[5]This Jour., 1919, p. 98.

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character of the work involved in solving the problem is not of a nature that lends itself to collaborative study. This much has been shown by what the committee has already accomplished, or failed to accomplish. It would also seem that the title does not adequately convey the meaning of what we are actually striving to determine. What we want to know is what effect hard water has in the tanning process. This broadens the scope of the investigation. The problem in the restricted sense of the effect of hard water upon tannin is of practical interest only to the producer of tannin extracts, and the evil effects of hard water for this purpose is appreciated fully. The loss of tannin in the tannery from the use of hard water is not an isolated problem but one inseparably linked with the entire process by which pelt is converted into leather.

Therefore, it is purile to attempt to master the problem by comparative analyses of tannin solutions made with distilled and hard waters. All the various elements and conditions that enter into the tanning process may have a bearing, direct or indirect, upon the tannin loss. It is even conceivable that hard water may effect no absolute destruction of tannin and yet entail a heavy loss to the tanner, and it is more than probable that the preponderance of loss is of this character. This loss comes from the repressive action of the salts that go to make hard water upon the acids, with consequent repression of the hide swelling. This function of salts has been very clearly demonstrated by McLaughlin[6]. That salts in tannin liquors were inimical to acids has been recognized for years, as has the repressive or mellowing action of non-tannins upon the astringency of tannin.

It is unlikely that the actual precipitation of tannin by the salts of hard waters will be proved of very great moment as the proportion of fresh water used is not excessive. If the character of the precipitate is such that it will remain suspended it will, to a considerable extent, be redissolved in the acid liquors and by dilution of the liquors from sappage, but in addition to the repressive action on hide swelling already referred to, it is likely that the salts will adversely affect the color, since it seems fairly well established that improvement in color is in direct proportion to hydrogen ion concentration.

[6]This Jour., 1921, p. 295.

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A suggestion for attacking the problem would be the installation of tanneries on a laboratory scale, running the check tannery with distilled water under conditions parallel to the smallest detail with the tanneries with hard waters. By accurate weighing of the pelt going in the tail, and of the liquor going on the head, and with transferring of equal volumes of liquor from head to tail and to sewer, with reservation of this latter for analysis, with, in fact, attention to all the details that is required for tannery control, it should be possible to ultimately determine fairly accurately the effect of a hard water.

And in the end, and to draw proper conclusions, analytical data will be required: liquor analysis, acid determinations, ash determinations, leather analysis, in fact, even more detailed information will be required than is usual in tannery control work. The official method of tannin analysis will be called upon to do its share in determining the effect of hard water in the tanning process, and called upon after the effect is operative and the results may have some real significance.

CONTRIBUTION FROM THE REED LABORATORIES.

BOOK NOTICES

PROCTER TASCHENBUCH FÜR GERBEREI-CHEMIKER. Translation from the English by Ing. Josef Jettmar. Second Edition. Price $1.00. Verlag von Theodor Steinkopff, Dresden and Leipzig.

Procter's Leather Chemists' Pocket-Book needs no introduction or recommendation to the leather chemist of experience. The original English edition was reviewed in this JOUR. 8, 221 (1913). This second edition of the authorized translation into German is true to the form of the original but contains an appendix which includes some corrections and elaborations for the purpose of changing the text to conform with the advance of our knowledge in the past seven years.

G. W. S.

TANNING MATERIALS. By Arthur Harvey. 182 pages. Crosby, Lockwood & Sons, London. Price 15 shillings net.

This book supplies a great need and will be welcomed by all. The author has assembled the available data on tanning materials and has arranged them in alphabetical order giving, in addition to the average reported composition, some important characteristics of the more important materials. In the discussion of the most important materials is given descriptions of methods of leaching and making of ex-

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tracts. The manufacture of tanning extracts is also treated of in a separate section. The water supply, handling and preparation of raw materials, different methods of leaching, clarification of liquors and various methods of evaporation are briefly described. A little more space is given to the newer processes of leaching and evaporation.

In Section IV is given the methods of examining tanning materials of the I. A. L. T. C., S. L. T. C. and A. L. C. A.

In Section V is given a few miscellaneous notes on extract manufacture, use of spent tan as a fuel and its value for other purposes

G. W. S.

ABSTRACTS

Old and New Ideas on Mixed and Rapid Tannage. ANONYMOUS. *Le Cuir*, 9, 598, 654 (1920); **10**, 34, 128, 178 and 248 (1921). With the unusual demands of the War, modern tannages came into prominence, and towards the last considerable leather by such processes was used for military supplies. It is believed that mixed tannage, that is the use of extract liquors as well as bark, will be the basis for future developments of French processes. While the introduction of extracts formerly may have been attacked by certain old school tanners and users it is rare now to find a manufacturer who will dispute the fact that with the new methods, leather of quality nearly equal to that by pure oak bark can be obtained. In some sections the old system still maintains its prestige because of habit and prejudice. Most of the latter can be attributed to failures by tanners lacking in scientific and technical training who tried to apply rapid tanning without adapting their methods to the new procedures and without putting aside old ideas and practices, hitherto considered indispensable, but which could be only a hindrance in accelerated tanning.

Some may claim that the old tanners made good leather without scientific training. This, while true, was not invariably the case, and many failures might have been avoided with more scientific knowledge. Furthermore economic conditions of to-day and the future will not permit the old extravagances in time, material and practices. In the old processes where the hides remained practically motionless for months in contact with the bark, tanning was very slow, being further retarded by the accumulation of non-tannins and insolubles with time. In the modern processes the hide is completely penetrated by suspension in liquors, followed by laying away for a time dependent upon the results desired, which together with an intimate contact of the hides and tanning liquors through agitation and frequent manipulation has effected an appreciable economy in time without injury to the quality of the leather.

Because of their influence on the resulting leather, the preliminary tanning processes must be carefully and rigidly controlled before any method of tanning will insure success. The usual methods of soaking and softening are described with particular emphasis on low yields from pro-

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longed soaking and liming, the use of putrid soaks, and excessive quantities of chemicals. To shorten the time for soaking very dry hides, alkalies are advisable. One kg. of caustic soda or 1.5 to 3 kgs. of sodium sulfide per 1000 liters of water may be used. Some tanners use hydrochloric, sulfurous, or weak solutions of other acids in the soaks which has the advantage of preventing loss of any hide substance but on the other hand requires more time.

One of the principal differences between the old and modern tannages, and one of great importance from the viewpoint of yield, is in plumping the hides. In the old processes, old limes were depended upon entirely for dehairing followed by new limes for the desired plumping. This invariably results in low yields through loss of hide substance in the old limes, the loss increasing with the age of the limes. For satisfactory yields and quality rapid liming and fresh limes must be used in the modern processes.

Whenever possible some means of heating the limes so as to maintain a uniform temperature and shorten the time in winter is very desirable. The modern use of sodium sulfide with lime is an excellent procedure since it materially shortens the time. Sodium sulfide alone for unhairing is not advisable and furthermore the lime is required to plump the hides and saponify the greases present and thus prepare the hide for tanning. The sulfide and lime should be carefully mixed so that the reaction will be complete, as otherwise green spots difficult to tan will be formed from the sodium sulfide. The sodium sulfide in either hot or cold solution should be mixed with the quicklime and the latter then slaked or the sulfide solution mixed with slaked lime while boiling the mixture with a steam coil. Vat liming may be done by either the three or five vat system. In the former each vat contains lime and sulfide and unhairing is done the third day, after which the hides are washed and put in fresh limes only for 24 to 48 hours. If one figures 2 kgs. of sodium sulfide to 18 kgs. of quicklime for a 7 to 8 cubic meter vat, holding 30 hides averaging 30 kgs., new limes can be prepared with 80 kgs. of quicklime and 8.8 kgs. of sulfide. For strengthening 7 to 8 kgs. of quicklime with the corresponding quantity of sulfide will suffice. Calculated on the hide weight about 10 per cent of quicklime is used with one-ninth as much sulfide. If the five vat system, which seems particularly appropriate for unhairing by suspension, is used, the strength of the limes is adjusted so that the unhairing is done the fifth day. In this system it is preferable to leave out the sulfide in the fourth vat and to have only fresh lime in the fifth one. In some instances unhairing by sulfide can be done in large drums. They must revolve very slowly and with as much solution as possible. The sulfide must be stronger than when vats are used. With this method however extreme care must be taken to avoid damage to the hide. Of all methods of unhairing that of painting the hair side with a dehairing mixture seems the most advantageous from the viewpoint of yield. With a paste of lime and sulfide

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unhairing can be done in from 2 to 6 hours. The hides must then be put in fresh limes for plumping and saponifying the greases. The mixture of lime and sulfide varies according to the hides. For certain foreign hides 40 kgs. of quicklime is mixed with from 15 to 22 kgs. of sulfide, the quantity of the latter depending upon the hides. When the hair comes out easily the dehairing may be done in drums with water, preferably lukewarm. They are then put for 24 hours in a bath of fresh lime of 4 to 6° Bé. This last method of unhairing, properly applied, permits the tanner to obtain the best yield of leather through shortening the time in the limes and thus avoiding all loss of hide substance.

For good yield of leather and good finish the modern tannages require radical changes in the deliming processes. Formerly deliming was not made a distinct operation, the tanner relying to a great extent upon the natural acids of the tan liquors to eliminate the lime so that deliming was accomplished simultaneously with the first stages of tanning. This procedure, while generally satisfactory with the long time tannages, has some inconveniences. Not only must the time of tanning be long but the first liquors soon become charged with lime salts and must be discarded causing the loss of considerable tannin. Furthermore the quantity of natural acid present varies widely making it necessary to frequently determine the acid to guard against the injurious effects of lime salts from insufficient neutralization or against too great an acidity in proportion to the tannin concentration and consequently loss of hide substance. Consideration of all this in the modern tannages, where shorter time especially in the first liquors and high yields are of first importance, has led more and more toward making deliming a distinct operation.

The use of stronger first liquors, made possible by extracts, has materially reduced the time but on the contrary the first liquors from extracts are deficient in the natural acids. To overcome this so that the lime will be completely neutralized and the hide be maintained in a suitable swollen condition to insure maximum absorption of tannin it has beeen found necessary to give the hides a preliminary acid bath and to artificially increase the acidity of the first liquors, thus making deliming a distinct operation.

Before the War, formic, lactic, and butyric acids were generally used but the latter has not been available since. In using, the acids for deliming, and especially the mineral ones, it is best to highly dilute them and to employ a quantity just sufficient for the lime, adding the required amount in three portions or better yet by following the deliming and adding as needed. It is absolutely necessary to guard against too much acid which would result in too great a swelling and brittle leather.

Contrary to general opinion sulphuric acid can be used for deliming but it requires very careful manipulation and also gives the difficultly soluble calcium sulphate. It probably serves best in the regeneration of weaker acids from their lime salts. Hydrochloric acid alone is not to be recommended because of its very rapid action and if not exactly con-

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trolled will give excessive swelling and any chlorides which may remain in the hide will produce flat leather. The best procedure for hydrochloric acid is with ammonia. Deliming, with stirring, may be done with 500 gms. hydrochloric acid for every 100 kg. of white weight after adding about one liter of ammonia. The ammonium chloride thus formed reacts with the lime so that a lime salt is formed and the ammonia and ammonium chloride continually regenerated. This method is economical and gives good results but is not as generally preferred as are the organic acids. Boric acid is recommended for quality, softness and good finish as it gives a nice color and a soft, silky grain. Being of very low solubility it can be used with safety. As it is expensive it is worth regenerating which can be readily done with sulphuric acid.

Of the organic acids, lactic is the most generally used. As it has considerable swelling power it must not be used in excess. From 600 to 900 gms. per 100 kgs. of white weight is the usual proportion. Formic acid has an advantage over the former in strength, since 46 kgs. of pure formic are equivalent for deliming to 90 kgs. of lactic. The criticism that formic acid is too violent is not sufficient to condemn it. The acid must not be added all at once but in portions and with frequent stirring of the deliming bath. The quantity of 90 per cent formic acid to be used varies with the results sought. For sole leather from 300 to 350 gms. per 100 kgs. of white weight is a good proportion, but the deliming should be tested, for example with phenolpthalein. Deliming may be done in vats, paddles, or drums. With the first the time is considerably lengthened requiring about three days according to the acid used. An often recommended procedure is that of using a latticed drum at very moderate speed.

While the swelling of hide, because of its importance, has been the subject of much study there is still a great divergence of opinions in the explanation of this phenomenon. Swelling is the absorption of a liquid by a solid body without any apparent chemical modification and is always accompanied by a gain in weight and very often by an increase in volume. Swelling may be the result of a capillary imbibition; or of endosmosis; or a molecular distension as with glue. The latter is, of course, of greatest interest to the tanner. Various investigators do not agree as to whether swelling is due to purely physical or chemical phenomena or to a combination of both. Van't Hoff is of the opinion that the water forms with the solid, a solid solution, an opinion shared by Procter. Vilhelmy believes that the water is absorbed upon the surface of the colloid in a peculiar state of condensation. According to Koerner swelling of the hide is due to chemical phenomena subject to certain thermodynamic laws. He proposes the following: (1) Upon immersion in water of a body susceptible of swelling it absorbs a certain quantity until it reaches a maximum. The maximum is greater in hides of young animals than in older ones; (2) The maximum depends upon the chemical nature of the material and liquid, the cohesion and elasticity of the former and the temperature and viscosity of the latter; (3) The swelling

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does not proceed uniformly throughout the mass as it reaches the maximum sooner in the external layers; (4) The volume of the swollen body is less than its original volume plus the volume of the absorbed liquid, the swelling being accompanied by a relative diminution in volume similar to that upon mixing certain liquids; (5) Swelling is accompanied by a disengagement of heat.

The necessity of tanning in an acid condition has been shown by the experiments of Schroeder. This must be borne in mind in deliming in the modern practice of using extracts almost entirely. The abundant natural acids present in the liquors in the old processes were sufficient to properly neutralize any lime in the hide but with extracts for the first liquors the tannin unites with the hide before the natural acids can develop and swelling can not be effected. While acidity can be obtained by the addition of acid, it is a delicate operation. In all cases during the period of swelling the hide should be in a tan liquor of constant or increasing acidity, never of decreasing acid content. In rapid tannage making use of extracts only, the hide must be perfectly delimed and in such a swollen condition as to assure the rapid and perfect assimulation of the tannin. The desirability and, in fact, the necessity for yield, fullness and firmness, of maintaining in the early liquors the swelling obtained in the preparatory processes has led to efforts to fix this condition by a preliminary treatment. For this purpose formaldehyde has been found very appropriate. It can be used by suspending the hides, before putting them into the tan liquors, into a weak solutions of two parts of formaldehyde per 1000 parts of water. This fixes the swelling, prevents the loss of hide substance because of its antiseptic properties, and gives a beautiful grain and good body to the leather. Kohnstein and others recommend a light tannage first of 1-2 days followed by a formaldehyde bath with the addition of an equal quantity (2 pts. per 1000) of hydrochloric acid. The skins are then thoroughly washed free of acid and can be put back into strong liquors without fear of cracky grain. With the use of formaldehyde one can tan almost entirely with extracts. The formaldehyde, though, must be used in weak solutions to prevent a brittle and drawn leather. The use of formaldehyde to fix the swelling of the hides, so that strong liquors may be used, must be carefully done with very weak solutions. Formaldehyde sometimes has an injurious effect which becomes evident after storage, producing brittle leather. The quinones, syntans, aluminum pyrophosphate and other special products such as viscous colloids can render the same service as formaldehyde without the harmful after-effects of the latter. The use of quinone and of the synthetic tannins, of the type of condensation products of formaldehyde and phenols or cresols, as a pretannage or mixed in the suspender liquors is very advantageous in the rapid tannage of sole, harness and belting leathers. They give to the leather a clear, uniform grain; fix the swelling; and hasten the tanning. Hides given a preliminary treatment with these can be put into strong liquors without danger of "drawn grain" or of "case hardening." It is essential that the hides be thoroughly delimed. The

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syntans however do not help increase the yield and should be considered simply as adjuncts to the tanning process. It should be noted that during the first days of tanning when using the syntans the grain seems to become drawn but this disappears later in the tanning.

R. W. F.

Notes on Leather Analysis. By RAFFAELE SANSONE. *Le Cuir*, 10, 396-8 (1921). Leather analysis is becoming of more and more importance to buyers and sellers in their transactions, to the tanner in control, to the shoe and belt makers in determining quality, and as a means of settling disputes. Because of its increasing importance it is well to consider any modifications of the method which may be advantageous. The value of proper sampling cannot be over estimated. When studying visible peculiarities in a lot of leather comparable samples should be taken of these and of the normal or best pieces as a control. A composite is generally made from samples taken in the back, near the legs, in the side and in the belly. When this is not feasible a single sample is taken in the neck which nearly approximates the average composition of the hide. The nature of the tannage is indicated and confirmed by comparison with known samples. The volume for specific gravity is determined by actual measurement of area and thickness or by mercury displacement in a graduated cylinder. The former method can be applied to whole skins without loss of leather. Moisture and grease content affect the specific gravity and for comparative purposes the gravity should be corrected to constant for these. To be exact correction should also be made for other constituents determined by analysis.

R. W. F.

Contribution to the Biological and Chemical History of Hides and Unhaired Skins. II. The Relation of Ammonia to Hide and Unhaired Skins. By W. MOELLER. *Coll* 614, 265-79 (1921). Little is known of the role of ammonia in the preparation of the hides for tanning and very few leather chemists even know that it is present in unhaired skins. Free ammonia is formed, however, during unhairing and plays an important part but, except in the process of sweating, it recombines at once to form ammonium salts or acid amides. Ammonia doubtless causes hydrolysis of hide substance and this hydrolysis, as is the case with lime or sodium hydroxide, is a function of the time, concentration and temperature. Its swelling action, however, is negligible. Collagen contains at most 0.4 per cent or 0.5 per cent of ammonia while a sample of hide powder was found to contain 1.56 per cent. This increase is due to fermentation of albumen during sweating or liming by the following bacteria: *Proteus Vulgaris, Bacillus liquefaciens, Bact. prodigeosum, Bacillus putrificus, Bactrytis bassiana, Penicillium crustacmus, P. brevicaule, Mucor Boidin, Phytophtora, Aspergillus niger, Isariafarinosa.* Although elastin is easily attacked during sweating or liming the albumin and globulin are first removed and then the elastin. After sweating only collagen and part of the elastin remains. The following experiment was carried out. 4.4

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gram portions of hide powder was treated with 100 cc. portions of 0.1, 0.5, 1, 2 and 8 N solutions of ammonia and filtered after 1, 3, 5 and 8 days respectively. The hide powder portions were dried and determinations made of the ammonia driven off by alkali. The filtrate was analyzed for ammonia and total nitrogen and from these results the amount of adsorbed ammonia and the dissolved hide substance was calculated. The results showed that ammonia hydrolyses hide substance and that the hydrolysis reaches a maximum with 4 N ammonia. The intact portion of the hide substance adsorbed a large amount of ammonia in the gaseous form, and this adsorption followed the adsorption law. There was no chemical reaction between the intact hide substance and ammonia, for hide powder which had been treated with ammonia and dried gave off less ammonia on treatment with sodium hydroxide than hide which had not been treated with ammonia. The hydrolysed portion of the hide substance partially reacted with ammonia to form ammonium salts or acid amides and the amount of this chemically bound ammonia was independent of the amount of hydrolysed substance, but varied with the concentration of the OH ions.

I. D. C.

The Structure of Chromium Salts. By G. Grasser. *Coll.* **616**, 356–67 (1921). Werner's theory of valency (New Ideas on Inorganic Chemistry, 1909) are applied to the structure of the basic chromium salts. Werner's theory is based on the assumption that a number of atoms may be bound to a central atom, either by principal or auxiliary valencies, forming a first sphere or zone. This group or radical can then bind other atoms which, with respect to the central atom, are in a second zone. The number of atoms in the first zone is known as the co-ordination number, and the maximum number which the central atom can bind in this way as the maximum co-ordination number. Molecules as well as atoms may be co-ordinately bound to the central atom. By a principal valence is meant one of the usual type, which binds such radicals as -Cl, -Na, $-CH_3$, etc. These are usually represented by solid lines. Auxiliary valencies bind together groups which can exist as independent molecules such as $-OH_2$, $-NH_3$, $-CRCl_3$ and are usually represented by dotted lines. Some of the more important types of chromium salts are given below. Potassium dichromate may be considered as made up of acid anhydrides.

$$\begin{matrix} O & & O \\ OCr\cdots\cdots & OCr\cdots\cdots & +\cdots OK_2 \\ O & O & \end{matrix} = \left[\begin{matrix} O & O \\ OCr- & OCr-O \\ O & O \end{matrix}\right] K_2$$

The tri- and tetra-chromates, $(CrO_3)_3.OR_2$ and $(CrO_3)_4.OR_2$, have similar structures. The ammonia and cyanide compounds,

$$Cr^{O_4}_{(NH_3)_3} \quad \text{and} \quad Cr^{O_4}_{(CNK)_3}$$

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show that there are three co-ordination places in chromium tetroxide. Its structure and that of the di-peroxide are therefore;

$$\begin{matrix} O_2 \\ OCr \\ O \end{matrix} \quad \text{and} \quad \begin{matrix} O_2 \\ OCr \\ O_2 \end{matrix}$$

Mixed salts of oxides and halogenides also occur as

$$\left[Cr\begin{matrix} O_3 \\ Cl \end{matrix}\right]NH_4 \quad \text{and} \quad \left[Cr\begin{matrix} O \\ Cl_4 \end{matrix}\right]R$$

The most important hydrates are the hexahydrates in which all of the neegative radicals are ionizable, such as $Cr\ Cl_3 + 6H_2O$ which has the structure $[Cr\ (OH_2)_6]\ Cl_3$ This, on heating, changes to the green hydrate which has one ionizable chlorine atom and the following structure;

$$\left[Cr\begin{matrix} (Cl.H_2O)_2 \\ (OH_2)_4 \end{matrix}\right]Cl$$

The intermediate hydrate, I, is known and a similar salt, the choloropentaquochromic sulfate, II, has also been prepared. Lately the sulfatopentaquochromic chloride, III, which does not produce SO_4 ions has been prepared.

$$\left[Cr\begin{matrix} Cl \\ (OH_2)_5 \end{matrix}\right]Cl_2 + H_2O \qquad \left[Cr\begin{matrix} Cl \\ (OH_2)_5 \end{matrix}\right]SO_4$$

I. II.

$$\left[Cr\begin{matrix} SO_4 \\ (OH_2)_5 \end{matrix}\right]Cl \qquad \left[Me(OH_2)_6\right]\begin{matrix} \cdot OH \\ \diagdown \\ \cdot SO_4H \end{matrix}$$

III. IV.

The probable constitution of sulfates with seven molecules of water is given in IV. Since the central atom can bind many different groups, various combinations may be formed such as the following series of sulfocyanides and of aquo-metallic ammonias.

$$\left[Cr(NH_3)_6\right](SCN)_3, \qquad \left[Cr\begin{matrix} SCN \\ (NH_3)_5 \end{matrix}\right](SCN)_2,$$

$$\left[Cr\begin{matrix} (SCN)_2 \\ (NH_3)_4 \end{matrix}\right](SCN), \qquad \left[Cr\begin{matrix} (SCN)_3 \\ (NH_3)_3 \end{matrix}\right],$$

$$\left[Cr\begin{matrix} (SCN)_4 \\ (NH_3)_2 \end{matrix}\right]R, \qquad \left[Cr\begin{matrix} (SCN)_5 \\ (NH_3) \end{matrix}\right]R_2, \qquad \left[Cr(SCN)_6\right]R_3.$$

$$\left[Cr\begin{matrix} OH_2 \\ (NH_3)_5 \end{matrix}\right]Cl_3, \qquad \left[Cr\begin{matrix} (OH_2)_3 \\ (NH_3)_3 \end{matrix}\right]Cl_3, \qquad \left[Cr(NH_3)_6\right]Cl_3,$$

$$\left[Cr\begin{matrix} Cl \\ (NH_3)_5 \end{matrix}\right]Cl_2, \qquad \left[\begin{matrix} Cl \\ H_2O \end{matrix}Cr(NH_3)_4\right]Cl_2,$$

$$\left[Cl_2Cr\begin{matrix} OH_2 \\ (NH_3)_3 \end{matrix}\right]Cl, \qquad \left[Cl_2Cr\begin{matrix} (OH_2)_2 \\ (NH_3)_2 \end{matrix}\right]Cl, \qquad \left[Cl_2Cr(OH_2)_4\right]Cl.$$

Another class of ammonias have more than one ring and are bound together by radicals the most important of which are, $:NH_2$:OH, :O,

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(NO_3), (SO_4). Examples of the compounds are $[(NH_3)_5\ Cr.\ OH.\ Cr.\ (NH_3)_5]\ X_5$ and $[(NH_3)_5\ Cr.\ O.\ Cr.\ (NH_3)_5]\ X_4$

In order to have a tanning action chromium salts must produce at least one chromium ion and must also be used in a medium in which they can ionize. The following basic salts, if we consider only two chromium atoms and whole OH groups, will be produced by the hydrolysis of chromium sulfate: $Cr_2(SO_4)_3$, $Cr_2(SO_4)_2{}^1/_2OH$, $Cr_2(SO_4)_3(OH)_3$, $Cr_2(SO_4)\,1{}^1/_2(OH)_3$, $Cr_2(SO_4)(OH)_4$, $Cr_2(SO_4)\ {}^1/_2(OH)_5$, $Cr_2(OH)_6$. The structure of the first member is probably $[Cr(OH_2)_6]\text{-}SO_4\text{-}SO_4\text{-}SO_4\ [Cr(OH_2)_6]$ for the blue and

$$\left[Cr\begin{matrix}(SO_4)\\(OH_2)_5\end{matrix}\right].SO_4.\left[Cr\begin{matrix}(SO_4)\\(OH_2)_5\end{matrix}\right].$$

for the green modification. The latter formula agrees with the fact that barium chloride precipitates only one-third of the sulfate and ammonia precipitates one part of sulfate with the chromium hydroxide. The correct formula may however be an asymmetrical one, $[Cr(SO_4)_3]$, $[Cr(OH_3)_6]$. For the second member two formulas are possible and experimental work only will show which is correct.

$$\left[Cr(SO_4)_3\right]\left[Cr(OH_2)_6\right].\left[Cr\begin{matrix}(SO_4)_2\\(OH)_2\end{matrix}\right]\left[Cr(OH_2)_6\right].$$

$$\left[Cr\begin{matrix}(SO_4)_2\\(OH)\end{matrix}\right]\left[Cr(OH_2)_6\right]$$

$$\left[\begin{matrix}(SO_4)\\Cr\ (OH)\end{matrix}\begin{matrix}(SO_4)_2\\(SO_4)_2\end{matrix}\right]\left[Cr(OH_2)_6\right]$$

The first formula does not express the low basicity and the stability of the salt, so a cyclic compound may be formed by a linking, through auxiliary valency, of the first and last chromium atoms. The structures of the blue, weakly acid form of the third member and of the green, slightly basic form are as follows:

$$\left[Cr(OH_2)_6\right]\begin{matrix}SO_4\\OH\end{matrix}\quad\text{and}\quad\left[Cr\begin{matrix}(SO_4)\\(OH_2)_4\end{matrix}\right]OH$$

The two possible structures of the fourth member are similar to those of the second member. The fifth member, which is very colloidal and only slightly soluble, can have one of the two following structures.

$$\left[Cr\begin{matrix}(SO_4)\\(OH)_4\end{matrix}\right][Cr(OH_2)_6]\quad\text{or}\quad\left[Cr\begin{matrix}(OH)_4\\(OH_2)_2\end{matrix}\right].(SO_4).[Cr(OH_2)_6]$$

The possible structures of the next to last member are;

$$[Cr(OH)_5]\ [Cr(OH_2)_6]$$

$$(SO_4)$$

$$[Cr(OH)_5]\ [Cr(OH_2)_6]$$

$$[Cr(OH)_4(SO_4)]\quad[Cr(OH_2)_6]\quad[Cr(OH_2)_6]\quad[Cr(OH)_6].$$

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Similar structures may be devised for the basic chlorides, but in all cases experimental work is necessary before the structures of these compounds can be considered definitely established. Chromium hydroxide may occur in three forms:

$$\left[Cr(OH_2)_6\right](OH)_3, \quad \left[Cr\begin{matrix}(OH)\\(OH_2)_5\end{matrix}\right](OH)_2, \quad \left[Cr\begin{matrix}(OH)_2\\(OH_2)_4\end{matrix}\right](OH).$$

The tanning intensity of the first, colloidal form is high while that of the other forms is slight. But the ionized portion is constantly replaced due to the equilibrium, so that the tanning intensity of chromic hydroxide is high.

I. D. C.

Chemical Problems of Dyes and Dye Works. By H. SCHWARZ. *Schweizerische Chemiker-Zeitung,* **37,** 433 and **38,** 449 (1920). *Coll.* **616,** 381-3 (1921). The color of a dye in the solid forms is influenced greatly by the size of the particles and also the color of the solid dye is seldom the same as its color in solution. The golden green irridescent crystals of diamond fuchsin, for example, give a dark blueish-red powder and a purple-red solution. The color of the solution is also influenced by the solvent and samples of the same dye may vary in this respect due to differences in the method of manufacture and purity. The color varies with the concentration of the solution due to hydrolysis, molecular dissociation, isomerism, or to the formation of compounds of dye and solvent similar to the hydrate of copper sulfate.

Every soluble colored substance is a dye to the solvent but not all colored liquids will dye solids. Dyes need not be colloidal in character but must be able to react or combine with the fiber. The dyeing action is greatly influenced by acids, alkaline or neutral salts, soaps, etc., and by the condition of the fiber. There is a difference in color and properties between the dye in solution and the adsorbed dye. The dye molecule after reaction with the fiber has undergone a change by which certain groups have again become active. A chemical theory of the dyeing of textile fibers in which the process is considered as one of salt formation has been worked out but an attempt is now being made to explain this process by the laws of adsorption and contact potential. No theory of the dyeing of plastic substances, such as celluloid, has been given in the literature but this may be considered as a special case of dyeing solutions if the plastic substance is considered as a "solid solution." Fastness to light is a property of the dye-fiber complex and not of the dye itself. Fastness is influenced by heat, dust, moisture, kind of light (sunlight or artificial), and by oxygen from the air. It is also increased by incorporating the dye with the substance, in case the substance is plastic, rather than coating the surface. These special problems can not now be worked out due to a shortage of dye works chemists.

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Tannins and Albumin. By Karl Freudenburg. *Coll.* **616**, 353-6 (1921). Baeyer and Villiger found that most weak bases have a tendency to react with phenols. Their results, with a few additional examples from the literature are given in Table I.

TABLE I.

	Phenol	b-Naphthol	o-Cresol	Resorcin	Pyrocatechin	Hydroquinone	Pyrogallol	Phloroglucinol	Catechin
Ammonia	–	–	–	1–1	–	–	1–1	–	–
Hydrazine	–	–	–	–	–	1–1	–	–	–
Diethylene diamine	1–1	–	–	–	–	1–1	–	–	–
Hexamethylene tetramine	1–3	–	–	1–1	1–2	1–1	1–2	1–1	–
Urea	1–2	–	–	–	–	–	–	–	–
Aniline	1–1	1–1	–	–	2–1	2–1	2–1	–	–
p-Tolvidine	1–1	1–1	–	–	–	2–1	–	–	–
a-Naphthylamine	1–1	–	–	–	–	–	–	–	–
Antipyrine	–	–	1–1	1–1	2–1	2–1	1–1	1–1	–
Quinoline	–	–	–	2–1	–	2–1	3–1	–	–
Pyridine	–	–	–	–	–	1–1	–	–	–
Quinine	1–1	–	–	–	–	–	–	–	–
Caffeine	–	–	–	–	–	–	1–1	1–1	1–

The first figure gives the number of molecules of the base and the second the number of molecules of phenol which combine. Many of these compounds are insoluble, especially if one or both components are difficulty soluble. Tannins are to be classed as difficultly soluble phenols, since in the crystalline condition they are only slightly soluble in cold water. In their relation to nitrogen bases, from ammonia to the complicated alkaloids, tannins resemble the simple phenols. Also in the formation of salts between phenolcarboxylic acid and nitrogen bases the phenolhydroxyls play a part. Tannins containing a carboxyl group react similarly.

The oxygen bases are very similar to the nitrogen bases and Baeyer and Villiger found that phenols and substances containing oxygen formed crystalline compounds entirely analogous to the compounds formed by nitrogen bases. Examples are given in Table II.

TABLE II

	Resorcin	Hydroquinone	Pyrogallol
Cineol	2–1		1–1
Oxalester		1–1	
Cinnamidaldehyde		2–1	
Dimethylpyrone		1–1	
Amylenehydrate (dimethylcarbinol)		1–1	
Trimethylcarbinol		1–1	
Camphor	1–1 & 2–1		

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The relation of phenols to oxygen bases as is the case with nitrogen bases, is unbroken from phenol to tannin. The following bases, which contain carbonyl oxygen, give a heavy precipitate with tannin in aqueous solution: cinnamic aldehyde, salicylaldehydemethylether, vanillin veratrum-aldehyde and dimethylpyrone. The formation of three layers on adding ether to an aqueous alcoholic solution of tannin is probably due to the formation of oxonium compounds of the ether and tannin. Starch which is precipitated by tannin, is bound to the tannin by the same group which causes the reaction with iodine. Tannin also combines with cellulose-like carbohydrates and probably with anthocyanins. If nitrogen and oxygen occur together in the same molecule as the salt-forming factors the nitrogen by no means has the preference. Pfeiffer showed that the compounds of zinc chloride and acidamides were oxonium salts. Also oxygen and not nitrogen is the connecting link in salts of urea and in the neutral compounds of aminoacids and polypeptides. By the above method it is possible to show the relation between compounds of simple materials and the precipitate of tannin and albumen which is the basis of leather formation. Phenol and urea form a crystalline compound. Also tannin reacts with different simple acid amides.

Diethylurea, asparagine, benzamide, and phenoxyacetamide give sticky precipitates at 0° C. with tannin solutions, while phenol and gelatine solutions also give a precipitate. Leather formation can therefore be followed back in the albumen component to the simplest amides and in the tannin component to phenol, and the salt forming power is in all cases the same.

The noticeable tendency of trivalent chromium to saturate itself with oxygen and nitrogen by forming addition compounds, with for example amines or urea, is the cause of its reaction with animal fibers.

While organic tannins must have a tendency to form hydrates or supersaturated solutions so that even crystalline members may be obtained in a colloidal condition, mineral tannins must in addition have a stable degree of oxidation in which addition compounds are formed. For this reason the stable trivalent chromium and aluminium are superior to iron or even cobalt.

I. D. C.

Process for Producing Ropes, Cords, Cables, Belts and the Like. Ger. Pat. 338,972. By G. Schmidt, *Ledertechn. Rund,* 13, 134 (1921). A process for the production of ropes, cords, cables, belts and tissues from all kinds of animal intestines characterized by only partly removing the mucous from the intestines steeped in lukewarm water and then while in the green state impregnating with lukewarm fish oil. Further operations are conducted in the usual manner. Or, the intestines with mucous partly removed and steeped in salt water are twisted or spun in the green condition, dried and then impregnated with lukewarm fish oil.

G. W. S.

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The Importance of the Micellar - Hypothesis of Von Nageli in Leather Research. By W. Moeller. *Ledertechn. Rund.* 13, 129 (1921). More than sixty years ago the botanist von Nägeli propounded a theory which is known as the micellar-theory in present day colloid chemistry. From the time of its inception this theory was contested and ignored. Recent investigators in colloid chemistry have accepted the theory and it is being confirmed more and more by X-ray investigations conducted on the principle of Laue. According to Zsigmondy the most essential concepts of von Nägeli can be briefly and comprehensively defined as follows:— "(1) Under micell in the broader sense is to be understood a molecular complex of the dispersed matter which is not penetrated by the dispersion medium. (2) Micell in the narrower sense is a crystalline, ultramicroscopic particle of the dispersed matter. (3) Micell-complexes originate by assembling of the micells to form ultramicroscopic and in many cases microscopic particles. (4) According to the manner of assembling, the micell-complexes form ultramicroscopic or microscopic particles permeated with the dispersion medium; or ultramicroscopic or microscopic colloid-crystals."

The author points out that this hypothesis has been almost entirely ignored in leather chemistry while it is finding extensive application in recent investigations in textile chemistry. This hypothesis was used by the author to explain the elementary structure of leather fiber. [See Die Elementarstruktur der Lederfaser, *Coll.* 577 to 584 (1918)]

G. W. S.

On the Question of the Use of Soda as Denaturant for Hide Salt. By J. Paessler. *Ledertechn. Rund.*, 13, 169 (1921). Recently several short treatises have appeared on the use of the most suitable hide salt to prevent the appearance of salt stains. The author calls attention to the fact that sufficient is not known of the nature of salt stains and the action of denaturing materials. Those hide and skin defects which always appear on the finished leather and are known as salt stains are not due to a single cause but to a variety. True salt stains may generally be due to two different causes—(1) Impurities in the hide salt like calcium sulfate and the like and (2) bacteria. It is possible that both go hand in hand or that the salt stains caused by bacteria can only be formed when the salt in question contains the necessary impurities. First, the formation of salt stains can be hindered by the use of salt containing the smallest possible amount of impurities of any kind, or by the use of the purest possible salt. Common salt alone has strong antiseptic properties and therefore the hide and skins should be salted as soon as possible after taking off in order to exclude completely the beginning of putrefaction. However this measure is still not sufficient to completely prevent the salt stains. If it is necessary to use a denaturant for hide salt it is advantageous to use one that will raise the antiseptic action of the salt. Soda

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has proved to be such and is added in amounts of about 3 per cent of calcined soda or 5-6 per cent of sal soda. Common salt is more favorable to the prevention of salt stains than rock salt. The Research Institute in Freiberg has been unable to find any disadvantageous effects on calf skins and cow hides by the use of salt denatured with soda in amounts given above, either in the properties or yields of leather. The use of zinc chloride as recommended by an American hide dealer gives no advantages over soda.

G. W. S.

PATENTS.

Catechin; Catechu-Tannic Acid. British Patent 161,431. E. H. BRAY, London. (Indian Wood Products Co., Ltd.; 8 Clive Street, Calcutta.). March 24, 1920. A process for the extraction of catechin and catechu-tannic acid from vegetable substances containing them consists in digesting the disintegrated raw material with hot water in the absence of air and preferably in an autoclave, filtering and concentrating the decoction, then cooling it in absence of air to allow the catechin to separate out, and finally evaporating the filtrate to dryness in absence of air and preferably *in vacuo* to obtain the catechu-tannic acid. The precipitated catechin is purified by washing with cold water and is then dried in the dark either by a current of hot air or by absorption of the contaminating liquid by means of sand contained in bags. As starting material, the wood of *acacia catechu* or *acacia sendra* and the leaves and shoots of *uncaria gambier* are mentioned.

Liming Hides. British Patent 163,109. E. C. R. MARKS, London, Feb. 10, 1920. In a liming and de-hairing process, the hide is first soaked in an aqueous solution weak in lime and mild in sodium sulphite, is then washed to eliminate the sulphide, being subsequently soaked in a stronger solution of lime only. The process may be conducted in stages in a series of vats as shown.

De-hairing Hides, Etc. British Patent 163,294. *Soc. Pichard Freres*, Paris. April 22, 1921. Hides with the hair or wool on, after being thoroughly dried, are momentarily immersed in liquid air, oxygen or nitrogen and after being drained for a few seconds are scraped or shaved to break off the hairs whilst still frozen and brittle, leaving the roots embedded.

Carrotting Hair, Etc. British Patent 163,297. *Soc. Pichard Freres*, Paris. April 28, 1921. A process for carrotting hair either whilst attached to the hide or skin or after removal therefrom consists in freezing the hairs after penetration by water, the production of ice in the interior causing the hairs to burst in places thereby improving their felting qualities.

Leather-Working Machines. British Patent 163,384. W. H. STAYNES, The Ferns, Belgrave, Leicester. Dec. 30, 1919. Relates to a rotary staking machine.

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The Editor has been notified that our bookbinders are compelled to increase the price of binding $0.60 per volume on all bindings. Therefore the price of bound volumes in exchange for unbound copies for the year will be $2.70 instead of $2.10 as formerly. We have also been advised that it is still impossible to obtain the leather as formerly used for half leather bindings for our journals.

A SOLUTION OF THE NON-TANNIN ENIGMA

By H. C. Reed

Rec'd. Dec. 1. 1921

In an article entitled "Theory and Practice of Leather Chemistry"[1] the following quotation from Faraday is given: "It is because our procedure was hasty, our data too few, and our judgment untaught that we fell into mistake: not because the data were wrong." With this the writer is in thorough accord, and also with the deductions drawn by the author of the article quoted from the saying of the eminent authority.

In a recent paper upon the effect of hard water upon tannin[2] it is shown that the criticism directed against the official method of tannin analysis by the author of the article upon theory and practice of leather chemistry was not substantiated by the data submitted: further, that the error predicted in the non-tannin determination, which was attributed to unequal distribution of the salt solution exterior to and within the hide powder, was refuted by the too few data offered.

In a further paper by the same author, entitled "The Non-Tannin Enigma"[3] analyses are submitted of various non-tannin components, in which it is shown that the hide powder by the

[1] This JOUR., 1917, p. 93.
[2] This JOUR., 1922, p. 26.
[3] This JOUR., 1918, p. 429.

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official method apparently absorbs varying amounts of the components: that the amounts absorbed are in every case, with exception of gallic acid, such as to leave a greater concentration in the unabsorbed than in the absorbed solution, and therefore a non-tannin result in excess of 100 per cent.

The inspiration for the investigation of the non-tannin enigma is attributed by the authors to a desire to establish a reason for certain results obtained by Alsop in analyzing a chestnut extract. The reader is referred to the article mentioned for these results.

A considerable study is under way in the author's laboratory on the question of improving the present method of tannin analysis, and it is hoped that some results of the investigation will be published in the immediate future. During the conduct of the work certain details came to light that pointed to the possibility that procedure was too hasty, or judgment untaught, in concluding that salts in pure water solution behaved in the erratic manner credited to them when in contact with hide powder.

The investigation required data on the solubles of wet chromed hide powder. It was found that although a relatively low blank might be given by the last wash water from the proscribed method of washing, say, 0.001 gram per 100 cc., that the same hide powder, in the proportion of 47 grams to 200 cc. of distilled water, agitated for ten minutes, gave a residue as high as 0.0083 gram per 100 cc.: that this residue, with the added residue from kaolin and paper might reach 0.010 gram per 100 cc. No claim is made for discovery of the fact cited. F. O. Sprague, in an article entitled "The Non-tannin Blank"[4] pointed out the possibility of error in non-tannin estimation from this source. It is however entirely probable that in analysis a certain proportion of the solubles of hide, as shown by blank determination with water, is precipitated by the tannin, and does not appear as non-tannin; but all the solubles from the hide powder are not thus removed. The residues from a number of blank determinations were combined and gave by analysis 63.5 per cent mineral matter, calculated on the dry residue. A nitrogen determination of an aliquot portion gave 16 per cent, calculated as hide substance leaving 20.5 per cent of organic matter present other than hide substance. There-

[4] This Jour., 1919, p. 103.

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fore the hydrolysis of the wet hide powder introduces a true error in the non-tannin item, not an imaginary one. The non-tannin blank residues taken up with a little distilled water are found to be strongly acid and quite highly colored, due no doubt to sulphuric acid formed by hydrolysis of the chromium sulphate of the hide powder. The odor is distinctly sweetish with a reminder of caramel. Chlorides are present from the hydrochloric acid used in deliming and acidifying the hide powder in the course of manufacture. The ash content of the absolutely dry and unchromed powder is 0.56 per cent and the lime content 0.28 per cent. Calculated to 12.5 grams of dry hide the lime figures 0.035 gram to 100 cc. of non-tannin solution. Washing does not remove all of the lime and some is found in the non-tannin blank residues.

With a water blank from the hide powder of the character shown it is most difficult to predict the effect that will be produced on the constituents of the non-tannins by evaporation. Immediately prior to dryness the sulphuric acid, owing to its concentration, may have a pronounced effect. It should invert sugars and caramelize them, and in the instance of cane sugar, later referred to, the blackening of the residue was most marked.

Whatever may be the reduction in residue weight from precipitation of soluble matters from the hide combining with tannin in the case of an official analysis of a tanning material, there can be no such compensating factor in the instance of a pure water solution of a salt. On the contrary it is conceivable that a salt solution may have a specific solvent action of its own tending to increase the blank above that for distilled water.

With 200 cc. of distilled water 5 grams of wet chromed hide powder, 73 per cent water, gave a residue of 0.0058 gram per 100 cc. with ten minute shaking: 47 grams of the same wet chromed powder gave 0.0065 gram residue under parallel conditions and 100 grams wet powder gave 0.0115 gram. Reagitation for a second ten minute period of the identical portions of hide powder with 200 cc. of distilled water gave only slightly less residue than that obtained from the first shaking, showing that the hydrolysis of the hide powder still continued.

In order to gain some idea of the non-tannin values of certain components of non-tannins by the hide powder method, solutions

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were made of the following materials in amount of 0.5 gram to a litre of distilled water: potassium sulphate, calcium sulphate, magnesium sulphate, sodium chloride and cane sugar. These dilutions were used since the greatest errors with the official amount of hide powder are found at the greatest dilutions according to the results shown in the article on the non-tannin enigma. The results obtained are given in the following table:

TABLE I.

Forty-seven grams wet chromed hide powder, 73% water to 200 cc. of solution of salts and sugar.

	Total solids	Non-tans official	Water blank	Non-tans corrected
Potassium sulphate.....	.0510	.0594	.0076	.0518
Calcium sulphate.....	.0547	.0600	.0076	.0524
Magnesium sulphate....	.0333	.0398	.0076	.0322
Sodium chloride.....	.0515	.0619	.0076	.0543
Cane sugar.....	.0471	.0501	.0076	.0425

Potassium sulphate and magnesium sulphate give results, when corrected by the water blank, in sufficient accord with the solids determinations to prove that no error exists in the non-tannin estimation with hide powder other than that due to the solubles of the hide powder. In the case of calcium sulphate it is interesting to note that, with the blank correction, there is an apparent absorption of the salt by the hide powder, implying a decrease in non-tannins, other things being equal, when this salt is present in tannin solutions. We would expect the calcium sulphate in solution to inhibit the diffusion of the calcium sulphate present in the hide, thus lowering the blank correction in this case. This substantiates the results obtained with a liquid quebracho extract by Wilson[5] and commented upon by the author.[6] Cane sugar, corrected for water solubles, gives an absorption of the sugar by hide powder, but as the cane sugar residue, as already noted, is pronouncedly affected by the sulphuric acid this is not surprising. Sodium chloride, after blank correction for solubles, shows an excess of non-tannins over solids, but in this case the complication of the interaction of sodium chloride and sulphuric acid enters. The replacement of Cl_2 by SO_4 would cause an increase in the residue weights, first because sodium sulphate

[5] This JOUR., 1919, p. 97.
[6] This JOUR., 1922, p. 26.

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weighs more than sodium chloride, and secondly because sodium sulphate holds water of crystallization. Further, sodium chloride, without blank correction, gives 120.2 per cent non-tannin, and if the time of shaking is extended to one hour the percentage rises to 125.4, indicating a specific solvent action of the salt solution on the hide powder. The non-tannin residues from all the salt solutions were darker in color than the corresponding solids residues, that from sodium chloride being the most intense and that from calcium sulphate the least intense in degree of discoloration. The cane sugar non-tannin was blackened and had a pronounced caramel odor.

Confirmative of the effect of a blank correction for solubles from chromed hide powder, let us assume that the error in the non-tannin determination of the potassium sulphate solution (Table 1) is 0.084 gram per 100 cc. (0.0594 — 0.0510 = 0.0084). Applying this blank as a correction to the potassium sulphate non-tannins, obtained by the authors of the non-tannin enigma with varying dilutions of the salt[7] we find the following:—

TABLE II.

Potassium Sulphate.

Concentration Grams per litre	Per cent non-tannins
10.00	102.5
5.00	102.2
2.50	101.4
1.25	99.7
0.63	99.9

Also, using their figures in the case of 0.63 gram per litre, we can calculate their probable blank and find this to be 0.0084, or closely corroborating the writer's figure. The proportionally higher percentages of non-tannins found in the greater concentrations may be due to a variety of causes and did not appear worthy of investigation, although such a result would be expected from the greater solvent action on the hide substance in the more concentrated solutions. Such concentrations are of no moment insofar as having any bearing on tannin analysis. A factor that may influence results is the effect that organic matter, of the nature of that from the solubles of hide powder, has upon the water

[7] This Jour., 1918, p. 433—Table III.

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of crystallization of salts in drying at temperatures between 98 degrees and 100 degrees Centigrade.

The problem presented as to the effect of the solubles of hide powder in the non-tannin determination of a tannin solution is a more complicated one. There enters in the interaction of the soluble hide and tannin, the effect of a strong mineral acid upon the components of non-tannins in evaporation and the influence of the mineral salts of the tannin solution. The amount of residue found in the blank tests with distilled water will vary with the degree of hydrolysis of the hide powder, plus the mineral matter removed from the hide powder, and the degree of hydrolysis appears from the following figures to be dependent upon the proportion of water to hide powder. A blank test from shaking 5 grams of wet chromed hide powder, 73 per cent water, with 200 cc. of distilled water was 0.0058 gram per 100 cc., while a blank test with 100 grams of the same wet chromed hide powder, under identical conditions, showed a residue of 0.0115 gram. The residue from 5 grams amounted to 0.23 per cent of the weight of the wet powder and from 100 grams to only 0.023 per cent. Thus the greater the proportion of water to hide powder the greater the hydrolysis. Now if, as in the tests submitted by Alsop[8] the 200 cc. used in the official non-tannin determination is diluted by addition of increasing amounts of water, the proportion of water to hide powder is increased and hydrolysis increased, producing increased non-tannins. By reducing the concentration of the tannin solution we do not affect the hydrolysis of the hide powder so far as the ratio of volume to hide is concerned, but it is likely that the hydrolysis of the hide powder is greater from a second and entirely different cause. For if we consider the specific effect of the tannin itself upon the hydrolysis, the greater the proportion of tannin to hide powder the less the hydrolysis. Yet a third factor to be considered is that the greater the proportion of hide to tannin the greater the absorption of non-tannin. When reducing the strength of the tannin solution yet keeping volume and hide powder weight unaltered our non-tannin should decrease somewhat by greater absorption of non-tannin, and at the same time should increase somewhat by greater hydrolysis of less tanned hide powder, the resultant

[8] This JOUR., 1919, p. 430.

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non-tannins being a compensation of the opposing forces. By reducing the strength of the tannin solution and the amount of hide powder in proportion, permitting volume to remain unchanged, we should increase hydrolysis and not alter the absorption of non-tannin. But another variable is introduced in the lowering of concentration. The less the concentration the less the astringency. This introduces the influence of time of shaking, since the less the astringency the greater the time required for equal absorption.

It is not purposed at this time to dwell to a greater extent upon the various influences controlling the results in non-tannin estimation, as a discussion of these is more properly pertinent to the question of the betterment of the method of tannin analysis as a whole.

It is admitted that in the instance of gallic acid there is apparently a very considerable absorption by hide powder. It is also true that gallic acid will convert pelt into leather, of a kind, and within a period less than is generally realized. Nevertheless, in the opinion of the author the present official method shows an absorption out of proportion to the value of gallic acid as a tanning material, although the absorption by hide powder is greatly reduced in the presence of tannin and it is manifestly unfair to draw conclusions from the analysis of a pure water solution.

In resumé, it would appear from the facts presented that the effect of certain components of non-tannins upon the non-tannin percentage by the hide powder method of tannin analysis cannot be said to be due to increased concentration of solution surrounding the hide fibers and decreased concentration of solution absorbed by the hide powder: that the soluble matters from chromed hide powder shown by a blank test with distilled water under conditions of analysis, are sufficient to account for the increase in non-tannins attributed to unequal concentration: that increased non-tannins in the analysis of tannin solutions, obtained by varying concentration, volume and weight of hide powder, may arise from a variety of causes, of which unequal concentrations of salts and sugars is not one: that gallic acid is a potential tanning material but absorbed by hide powder in proportion not truly representative of its value: that the effect

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of hydrolysis of hide powder upon the non-tannin determinations should be thoroughly investigated.

In reference to the question of hydrolysis of hide powder reference is made to the article by W. Moeller, entitled "The Proteolytic Factor in Tannin Analysis."[9]

References is made also to the article by C. R. Smith.[10] The investigation is upon osmosis and swelling of gelatin, and the conclusion is drawn that the Procter and Wilson assumption that the hydrogen-ion concentration of the jelly is always less than that of the external solution is incorrect: that it appears incorrect to consider a lump of jelly as a phase distinct from the surrounding liquid: that the bulk of the enmeshed liquid in the jelly has the same concentration of electrolytes as the exterior liquid.

The author takes the opportunity of expressing his appreciation of the valuable assistance rendered by Dr. T. Blackadder in connection with this investigation.

CONTRIBUTION NO. 4 FROM THE REED LABORATORIES.

ANTHRAX PROPHYLAXIS IN THE LEATHER INDUSTRY*

By Alfred Seymour-Jones

Like many other diseases, anthrax is due to a micro-organism, in this case the *Bacillus Anthracis*. This has two stages of existence, the vegetative or active short rod-like form, which is the state in which it is found in the blood of infected humans and animals, and the spore or egg-like condition. This latter stage of its existence is the source of incidence of the disease among humans and animals. It is necessary to point out at this stage the not unknown fact that, in the rod-like or live and active form, disinfection may be carried out with comparative ease. Drying alone will kill the rod bacilli. Our concern is with the spore and the means of sterilising it in infected material such as hides and skins.

For many years the medical side of the Factory Department of the British Home Office, under Dr. T. M. Legge, have made a close study of the provenance of the materials conveying anthrax

[9] *Coll.* 603, 307-19; 604 374-81; This JOUR., Abst. 1921, p. 163.

[10] *J. A. C. S.* 43, 1350 [1921) This JOUR., Abst. 1921, p. 649.

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to industrial workers. Their observations and statistics as applied to the British Isles are of great value to a country like the United States of North America where the conditions are very similar. The British Ministry of Agriculture have likewise, through their chief veterinary officer, Sir Stewart Stockman, collated and tabulated evidence and statistics of great service concerning the incidence of anthrax among cattle. This information from these two departments together with my own researches of over thirty years form the basis of this paper.

Anthrax is a disease which is imported into countries like the United States and Great Britain, and, being imported, its entry can be prevented. Having learned how and in what way it enters, it is necessary to study if it is at all possible to devise means which will either reduce the risk of infection or will entirely prevent its entry.

The materials which act as conveyors of anthrax spores are hair, bristles, wool, and dried hides and skins from certain known countries, mostly those generally spoken of as "Eastern." It is of great importance to note that we possess no clear evidence against wet salted hides; they can therefore be dismissed from consideration for want of incriminating evidence.

For many years past there has existed at Bradford (England) an "Anthrax Investigation Board," who, through their bacteriologist, Dr. F. W. Eurich, and his staff, have conducted prolonged researches into the incidence of "wool sorters' disease," which is anthrax in its pulmonary form, and into its prophylaxis. Dr. Eurich conclusively proved that the dried blood clots, found in certain types of fleeces from given countries, were the true carriers of the anthrax spore. After many experiments on a laboratory and a bulk scale, a method of sterilizing wool, hair, bristles and the like, was discovered. This method is known as the "Duckering Disinfection Process" and has been adopted by the British Government. The first plant has been erected in the port of Liverpool and is in full operation. Its description is set out in the Home Office memorandum as follows:—

"In the practical application of this process it is proposed to use modified wool scouring and wool carbonizing machinery so arranged that no intermediate handling of material is required. In

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the preliminary treatment the material is submitted to the action of an alkaline solution of soap, maintained at a temperature of 102° F. (39° C.), for 30 minutes in three stages of 10 minutes each; and in the disinfecting solution of formaldehyde, also maintained at a temperature of 102° F. (39° C.), for 20 minutes in two stages of 10 minutes each. It is then dried, cooled, and rebaled."

The formaldehyde solution is 2½ per cent. The grease washed out is subsequently recovered. The estimated cost of disinfecting each pound weight of wool is given at 2.75196 of a penny, but it is hoped that this cost will be reduced with greater experience in working. The plant has been in operation for some months past with success, but it is as yet too early to give reliable statistics.

It is the intention of the British Authorities eventually to erect disinfecting plants at the ports of shipment when the system has been proved and when the economic condition of the world settles down.

It will be observed that the Duckering system depends on a given temperature, which is one suitable for softening the blood clots and hatching out the spores into the rod-like form. At the critical point of hatching out they are in a soft and delicate state, ready for the formaldehyde to complete their death. I see no reason why that system should not prove eminently successful in preventing the disease among wool, hair, and bristle workers.

The statistics of the Home Office Factory Department are conclusive in regard to dried hides and skins from certain countries as being the carriers of anthrax spores, but, so far as I have been able to learn, they have no records of anthrax infection among humans coming from sun dried hides. It is extremely probable that if such hides had been infected the ultra-violet rays of the sun would destroy such infection. It is generally realized among bacteriologists that sporulation of the bacilli can only take place in the dark or deep shade at a suitable temperature and under suitable conditions. I have repeatedly attempted to obtain sporulation in daylight, without success, and Dr. Georges Abt had similar experience at the Pasteur Institute, Paris, while working on anthrax. Sporulation is possible if the light be filtered through suitable red colored glasses which cut out the ultra-violet rays. These are, for our purpose, interesting observations.

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When considering any method of disinfecting dry hides or skins it must be remembered that any *such method must not injure the hides and skins or interfere in any way with the subsequent processes through which they may pass when being converted into leather.* That condition accepted, we are at once denied the employment of any system interfering with the hides' natural condition. Dry sterilization of hides may be dismissed as quite impracticable. The spore is extremely resistant to all disinfectants while wet, and entirely so when dry. This brings us face to face with the fact that the first step must be the restoration of the dry hide to as near its original wet condition as possible. The known methods of soaking back dried hides are the stale soak, alkaline solutions, and the acid process. The safest of these is the acid method. This process has been largely adopted throughout the leather industry since I called attention to it some twelve years ago for softening back dried hides. Blockey and others have carried out researches into the question of loss of hide substance and their results tend to show that the loss by this method is so small as to be negligible; it shows a gain over all other methods. In practice any of the organic acids are used, formic or acetic for preference. The strength varies from one-fiftieth to 1 per cent, and the period of time required varies from twenty-four hours to three days, according to the class of hides and the temperature.

In softening dried hides by the acid method, the entire dirt, filth, etc., which has either been plastered on the flesh side or accumulated in transit, disappears, giving a clean white hide both as to flesh and hair, and exposing all the damages, such as flesh cuts which the innocent native has so carefully covered up to defraud the guileness white man.

It may be submitted that the mere softening down of dry hide or skins does not entirely exclude the element of infection, which is limitedly true; it does, however, as I shall show, exclude infection of cattle.

In order to carry through any scheme of disinfection of dry hides, we are limited as to the agents to be employed. It must be borne in mind that the hide must not be injured in any way. Formaldehyde and its allies are excluded because they tan the hide. The carbolic series, even if effective, are excluded for the

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same reason. In many years of research I have tried all the known and many of the problematical disinfectants, and have had to fall back on mercuric chloride. Using various amounts, my experiments went to show that whatever the quantity of that salt employed in the presence of an acid it did not become fixed but could be freely washed out in the usual washing process before the hides were placed in the unhairing limes. This observation is confirmed by the work of Loeb and others. But if the mercuric chloride was employed in conjunction with an alkali for softening, then it became fixed by the hide, and could not be removed by simple washing, leading to dark stains in tanning.

Innumerable experiments were made on the foregoing lines with anthrax spores of varying virulency under every conceivable condition in which it was thought that the spores might occur in hides. It was found that the spores are always superficial and not buried within the hide structure. By superficial I mean that they are always found in the excreted material, blood, etc., adhering to the hide. This matter is attached either to the hair or to the pelt and may be scraped off with the finger nails or some sharp instrument. This fact has been noted by other workers.

There are numerous methods by which sterilization may be accomplished, but they all interfere with the resulting product. By accepting the rule laid down, it follows that hides so treated and uninjured will find a market against any ordinary uninfected wet-salted hide.

In the mercuric chloride experiments on the acid softening lines, when employing a strength of one per three thousand, the spores were found to be completely sterilized, and later tests went to show that one per five thousand would reasonably secure the desired end. The final method which I suggested was to employ a solution of formic acid of one per cent strength, which may be reduced in practice to a half per cent or less, and add thereto one part per five thousand of mercuric chloride in a pit of water. In this the hides are immersed, being stirred occasionally with a pole so as to present all surfaces to the liquor. In from 24 to 96 hours they swell to about their former wet state; they are then immersed in a pit of saturated salt brine for an hour, drained, and baled up for shipment. The cost of the process under the most trying financial conditions would work out at about six cents per hide.

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Such hides would be wet salted. The operation should be carried out at the port of export and not at the port of import for reasons which are obvious and for another to be mentioned immediately.

The value to the tanner of such a process lies in the elimination of a gamble in buying dry hides. At present they are so skilfully plastered with "real estate" that it is impossible to form any estimate of their value. The exporter would gain because he would at once see that he had paid too high a price for the hides which are badly flayed or "hazelled," and indirectly the scheme would do much to induce the native to flay the hides properly. Other reasons for its adoption will naturally suggest themselves to the exporter and tanner, but I place the demand for some such method on a higher plane. The death rate among humans is a strong argument and the death rate among cattle equally so. Once introduce the anthrax spores into our countries, we lose all control over them, as is evidenced by the deaths from that disease, a postman, a school teacher, a barman, a school girl, housewives, and many other people who are totally unconnected with the usually recognized sources of contagion. Setting aside the mercantile demand for sterilization, let us demand the prevention of all diseases which are importable and from which humans and animals receive either ill health or death.

The case against dry hides indirectly infecting living cattle has been proved beyond doubt in Great Britain. In those Isles the stock raiser relies largely on imported feeding stuffs to feed his herds. Such feeding stuffs are made from soya beans, linseed, and similar oil producing cereals. We have evidence of such seed stuffs being carried in the same ship with dry hides, and both cattle and workers have contracted anthrax from the cargoes. More extraordinary evidence still is to be found in the Ministry of Agriculture's statistics relating to the incidence of anthrax among cattle in its relation to importations of artificial feeding stuffs. As the use of artificial foods decreased, so did the incidence of anthrax among cattle decrease. During the Great War, Britain was prevented from importing artificial foodstuffs, and the incidence of anthrax among cattle almost vanished.

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What happens is very much as follows:—The dry hides are in bales and are shipped from the same countries supplying the seeds or beans for the production of artificial feeding stuffs. During the voyage the rolling of the ships cause the bales of hides to oscillate, thus the surface matter, in the form of fine dust, charged with anthrax spores, gets into the ship's atmosphere and settles down among the beans. Although these beans undergo great pressure in expressing the oil content, and are subsequently boiled, the spores resist the sterilizing influence of such treatment, only to carry the infection to such cattle as may happen to eat of them. On the other hand it is quite possible and probable that the beans may be infected before shipment in the Go-downs or in transit from the interior in river boats also carrying hides. This is a risk which must be taken during the early days after some scheme for the disinfection of hides has been put into force, and will decrease as time goes on for the native, who is keenly alive to obtaining the fullest values for his hides will wet salt his hides immediately after flaying. This, if done to anthrax infected hides, will sterilize the bacilli.

The Formic-mercury process of sterilizing infected hides and skins has been investigated as to efficiency by many scientists on laboratory lines. Dr. Constant Ponder made a prolonged research into the general question on behalf of the Leathersellers Company of London, one of the ancient trade guilds. Dr. Georges Abt, of the Pasteur Institute, Paris, made a similar investigation on behalf of the French tanners. Both these gentlemen are experienced in leather industry conditions and long reports were issued detailing their results. Both reported in favor of the Formic-mercury process. Others also followed suit with similar results. Others pointed out that the weak solution of mercuric chloride did not completely kill the spores as they could be revived after treatment with sodium sulphide, but that if the strength were increased the process was effective. Others condemned the process and pronounced in favor of the Schattenfroh process of pickling the hides by first giving them a bath of 2 per cent hydrochloric acid in water at blood heat and then heavily salting them. This process I tried over twenty-five years ago and abandoned because it did not comply with the conditions I have laid down. It is effective because it relies on the hatching out process at blood heat.

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The industry should not consider any method of sterilizing hides and skins which reduces their competitive value in the open markets of the world, and it is the bounden duty of tanners to see that they are not guilty of importing disease into our midst. In the Formic-mercury process I have absolutely no financial interest. The labor has cost me more money than I care to calculate and the results have been given freely for the benefit of mankind throughout the world.

It is over ten years since I published my results and there has been ample opportunity for a thorough investigation of its merits by scientists and the trade. Scientists disagree as to its efficiency when employing one five-thousandths mercuric chloride, unless the hides are not subsequently treated with sodium sulphide. This suggests that where and when hides so treated have been brought to a tannery they should not be subjected to sodium sulphide. On this point Dr. Abt says:—"The method of Seymour-Jones would give appreciable results, provided the depilating be done with pure lime, or lime sharpened with arsenic sulphide, or perhaps again with very concentrated sodium sulphide." Such a condition might form part of any government regulations.

In regard to the hatching out process already mentioned, those who like myself have studied this problem in the eastern countries like India, Indo-China, and China, know that during the major part of the year the temperature of cold water drawn from such usual sources as rivers is very high, sufficiently high to carry forward the hatching out process

The period of time between the soaking back and salting before the hide bundles arrive at the port of sale would probably be from six weeks to two months, during which time they will have lain in the swelteringly hot hold of the ship through the tropics and semi-tropics, again calling into action the hatching out process.

It will be seen from what has been said that *any system* which restores dry hides to the wet salted state is a sure method of preventing infection among cattle. If the small quantity of mercuric chloride as stated be added to the acid soak liquor, then immunity among workers is assured provided the hides are not submitted to weak sodium sulphide. Dr. Constant Ponder, who is well qualified to speak on behalf of the Leather Industry, wrote in the *Lancet*

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(1911):—"A practical method (the Formic-mercury) having been suggested, how can its application be ensured to those goods which constitute a potential danger to our workmen? The American Government has led the way by making it illegal to import hides and skins into their country unless accompanied by a Consular certificate stating that there is no anthrax among the cattle in the district from which they are imported or that the goods have been submitted to a disinfecting process. As regards the first requirement, it is ineffective because the skins come to the port from far inland, whilst the second is useless because no effective disinfecting process is suggested.

"Civilized Governments should forbid the importation of hides or skins unless either (1) they have been submitted to the ordinary 'wet-salting' process immediately after flaying; or (2) if cured by drying they have been converted back to the 'wet-salted' state by the 'Formic-mercury' process before leaving the country of export. If such regulations were adhered to I am convinced we should hear no more of anthrax among the dock labourers and warehousemen in Bermondsey and Liverpool, nor of those sporadic cases which are continually cropping up in the tanneries in different parts of the country."

These words are endorsed by numerous scientific men whose opinions are respected throughout the leather trade of the world.

It is pertinent to ask the question "If some such scheme be adopted, will it be a success?"

The scheme mentioned at the outset for sterilizing wool, etc., which has been started in Great Britain is yet too young to quote figures. The only clear case of which I know is that of New Zealand. Previous to 1905 that country experienced repeated outbreaks of anthrax. New Zealand is not a hide importing country; rather does it export hides and skins. Therefore the cause was sought for and found in other animal substances which were being imported, to wit, manure. In 1905, the Governor, by Order in Council, issued a Regulation, too long to quote, whereby no manure of any sort from certain countries could be imported without first undergoing a temperature of 281 or 267 degrees Fahrenheit, and fifty or forty pounds pressure, for three or two hours, before shipment. All shipments were subjected to rigid

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inspection with issue of certificates. The charges fall on the exporter. Here we have a most drastic order and an expensive system, entailing a somewhat elaborate plant. That order came into immediate operation with the following result. In 1906 and 1907 two cases of anthrax, in 1908 none, and in 1909 one case of anthrax were reported, but the latter was not certified. These cases were probably due to left over manures. *Since 1909 no case of anthrax has occurred in New Zealand.* With the example of New Zealand before us, surely for the sake of humanity the United States and Great Britain will bestir themselves to prevent the importation of this fell disease. Scientific sanitary cordons have been established around our lands. Let them be however high, they do not, cannot, and will not prevent disease from being imported unless the prophylaxis is tackled at its root, the port exporting such disease.

The Great War for Liberty has been fought and won. Great Britain and her Dominions overseas gave the lives of over 947,000 of their finest young sons, and over 3,000,000 wounded, for the cause. The United States, during the time they had the honor of fighting, gave more of their best and dearest in proportion for their great inheritance of Liberty. Have they died in vain? Our finest scientific brains fought the enemy, death, which lurked in the trenches, and won. Are we liberty loving people going to allow a deadly enemy like anthrax to stalk our sons at their labor for daily bread? Are we going to permit it to continue its depredations? The United States has led the world in "Safety First." Will it take the initial steps to combat anthrax and other evils from coming among us? Up to now it is the worker that has suffered from anthrax, and not the rich man or woman. The life of the humblest worker is just as great an asset to the nation as the King or President, and it is a nation's bounden obligation to take the greatest care of all stages and conditions of life, whether human or animal.

In conclusion I submit that this meeting of scientific men should put such pressure on the authorities, tanners and governmental, as will cause them seriously to consider the whole question *de novo.* Any action taken by the two great English speaking nations will be followed by the rest of the world. Any assistance

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I can give to accomplish this desired end, be it by the Formic-mercury process or any other acceptable method, is at the disposal of humanity.

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WREXHAM, N. WALES.

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ABSTRACTS

Wattle Bark Tannin. By R. O. Phillips. *Hide and Leather*, Nov. 5, 1921; p. 57. A discussion of those plants classed under the name of wattle with particular reference to those which have the most importance because of the tannin content of their barks. All of the important wattles in this respect are indigenous to Australia where the bark has been utilized in tanning for a long time. The tree was introduced into South Africa where it is now grown on a large scale for its tan bark. The three most important wattles cultivated in South Africa for tan bark are: the black wattle (*Acacia decurrens*), the green wattle (*A. decurrens*, variety *mollissima*), and the golden wattle (A. pyonantha).

Wattle bark tannins are of the catechol class. The extract is fairly astringent, very soluble, of high purity, and is claimed to be a rapid penetrator. Alone it is claimed to produce a smooth, even grain of uniform color. In Australia wattle is often used alone for tanning but elsewhere it seems that the best results are obtained by blending with other materials. Some materials with which wattle has been used are myrobalan, valonea, hemlock, oak bark and quebracho extracts.

Leather tanned with wattle is said to have a high tensile strength and considerable elasticity.

The author gives the results of the analysis of wood of the black wattle. The tannin content of the wood is very low, ranging from 0.1 per cent at the base of the tree to 1.89 per cent at the top which is the reverse of the condition found in the bark where the tannin content decreases from the base toward the top of the tree.

Mechanical Flaying. By P. Gourlay. *Le Cuir*, 10, 447 (1921). It is safe to say that defective flaying occasions more loss of value to the hide trade than anything else. Knife flaying causes an estimated annual loss of 8 to 10 million pounds sterling in Europe alone. The apparatus described in this article consists of an electric motor, suspension for same, a flexible transmission, and the flaying tool proper. The motor is constructed to run freely on an overhead trolley. It is arranged for direct current, but is fitted with a short circuit interrupter for alternating current. It is completely protected from dust and water, being in a hermetically sealed box, and is damp proof. It has a special starter and a new type joint for connecting with the flaying tool. The motor supplies one-sixth horsepower and consumes 180 watts per hour. The flexible transmission is somewhat similar to the type used by dentists, but much stronger. It is 2½ yards long and allows considerable latitude in the use of the tool. The flaying tool is about the size of the hand and is fitted with a shield and milled grip. The shield encloses a three-winged toothed fly wheel, which is caused to rotate rapidly. It makes about 3,000 revolutions per minute and the teeth are blunt so as not to cut the hide or be dangerous to the operator.

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The tool, which is known as "Perco," is very simple to operate. Any unskilled hand can flay a hide in from 10 to 20 minutes. The head and forelegs are flayed with the knife and the hide opened up with the knife and removed sufficiently to get a good hold on the edges with the hand. The flaying tool is then used being held flat against the flesh.

The Analysis of Partially Hydrolyzed Fat. By W. Fahrion. *Chemical Umschau Geb. Fette, Oele, Wasche, u. Harze*, **28**, 68 (1921); through *Ex. St. Rec.* **45**, 614 (1921.). For determining the amounts of neutral fats in partially hydrolyzed fats the following method is suggested:—

A weighed amount of the fat is heated with alcohol and the acid number determined. A given amount of alcoholic base is then added and the saponification number determined with the help of a blank test. The resulting neutral soap solution is made alkaline, diluted with 50 or 20 per cent alcohol, and the unsaponifiable fraction shaken out with ether or petroleum ether. The neutral fat is then calculated from the formula $X = \frac{(100 - Y) \times \text{acid number}}{\text{saponification number}}$, where Y = the determined percentage of unsaponifiable matter and $100-(X+Y)$ = the neutral fat.

Research Problems in Connection with the Leather Belting Industry. By J. Edgar Rhoads. Address before the National Association of Leather Belting Manufacturers, Nov. 16, 1921. *Hide and Leather*, Nov. 26, 1921. Two common sources of trouble with leather belts are stretching and running crooked. Stretchiness depends on the kind of hide and methods of tanning and currying as well as on the thoroughness with which the leather was stretched before it was made up. Running crooked is apt to be caused by one edge of the strip drawing up more than the other after it has been stretched and cut to width. This is more apt to occur with leather which is not very thoroughly tanned. With moderate tensions, stretch is not such a serious matter, but the tendency of recent time is to increase tensions so as to transmit more power with a given size of belt.

Creeping is closely allied to stretching. It accounts for about three fourths of one per cent of what is measured as slip. The belt is stretched more on the tight side than on the slack side. This difference causes the belt to creep on the surface of the pulley. The coefficient of friction varies with the rate of slip and with the kind of surface, but not much with different tensions. Tensile strength is not of the highest importance in the case of leather belts because the factor of safety is always high, from 5 to 10.

The relation of belt speed to power transmitted is an important factor. At high speeds centrifugal force lessens the pressure against the pulley. The greatest efficiency lies between 4,000 and 5,000 feet per minute. The effect of slip on coefficient of friction at high speeds has not been investigated. High humidity of the atmosphere lowers the effectiveness of a leather belt.

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Variation in load must be met by increased size of belt. Authoritative figures on this problem are needed. The effect of arc of contact and center distance on belt performance also need further investigation. In the case of horizontal belts, the question of running the tight side at top or bottom has not been answered with sufficient definiteness. It has been shown that in general better results are secured by running belts with the grain side to the pulley. Comparisons of the power transmitting capacity of leather belting with the principal substitutes have been made by at least three investigators. Leather belts are distinctly superior to any substitute, especially in the cases of overload and shock load.

L. B.

Conditions Affecting the Quantitative Determination of Reducing Sugars by Fehling Solution. Elimination of Certain Errors Involved in Current Methods. By F. A. Quisumbing and A. W. Thomas. *J. A. C. S.* **43**, 1503 (1921). The errors involved in all attempted improvements upon the original method are (1) reducing action of sucrose, (2) "blank" or auto-reduction of Fehling solution, including all modification of same, and (3) lack of exact temperature control. The two minute boiling method does not ensure control of temperature because of variations in atmospheric pressure at different times and places. A variation of 2 per cent in the reducing power of 100 and 150 mmg. of dextrose is reported between determinations made at 753 and 760 mm. pressure. Reduction increases with increase in temperature and time although it appears to be complete at temperatures below 90° C. after 1 hour's, heating. At temperatures above 100° there is an appreciable increase in reduction which may be due to auto-reduction of Fehling Solution. Auto-reduction is completely absent at 80° for periods up to 30 mins., and at this temperature there is but slight formation of cuprous oxide even after heating for 1 hour. A study of Fehling solution from the standpoint of the nature and concentration of alkali, concentration of copper sulfate and Rochelle salt to find the maximum and minimum concentrations of these substances necessary to give the greatest yield of cuprous oxide and to ensure the formation of complex cupric tartrate ion lead to the adoption of the following solution:— (1) Copper Sulfate Solution—Twenty-five cc. to contain 525 mmg. of copper or 41.2 g. of cupric sulfate pentahydrate in 500 cc. of the solution. (2) Alkaline Tartrate Solution:—*Sodium hydroxide.* A saturated solution prepared from sodium hydroxide (purified by alcohol) let stand for several days until insoluble carbonates and other impurities settle out. The clear solution siphoned off and its alkalinity established by titration. *Crystallized Rochelle Salt.* One hundred and seventy-three g. (highest purity) dissolved in water in a 500 cc. graduated flask and the calculated amount of sodium hydroxide solution added, so that 500 cc. of solution contains exactly 65 g. of sodium hydroxide.

A study of surface oxidation involving different methods of heating and receptacles of various sizes was carried out in order to determine the

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amount of copper lost due to surface oxidation which showed that the loss of cuprous oxide due to this cause can be obviated by either covering the liquid with some inert liquid as toluene, or by covering the beaker with a watch glass. The catalytical effect of the walls of the container was studied and it was demonstrated that the greater the lateral area of liquid exposed to glass the greater was the reduction, that is, a reduction carried out in a 250 cc. beaker yielded much more cuprous oxide than the same amount of solution when reduced in a 750 cc. beaker (diameter of the vessel increasing with its size.) The area of the bottom of the vessel does not appear to have a material effect in this respect.

The authors adopt the following procedure which eliminates most of the sources of error in such a determination:— Measure accurately 25 cc. each of the copper sulfate and alkaline tartrate solutions into a 400 cc. Pyrex or Bohemian glass beaker, the diameter of which is about 9 cm. Add 50 cc. of sugar solution making a total volume of 100 cc. Cover the beaker with a watch glass and place the beaker in a water-bath which is maintained at 80°. After exactly 30 minutes' digestion, filter the cuprous oxide by suction through a mat of asbestos in a Gooch crucible. Wash the precipitate in the usual manner. Weights of the sugars to be taken for analysis. For dextrose, levulose and invert sugar, take 50 to 150 mg; for lactose and maltose, take 100 to 300 mg. These weights of sugars will reduce about 100 to 350 mg. of copper. Sugar table is given for obtaining the weight of sugars from the weight of copper or cuprous oxide obtained by this procedure. The equations for the calculations are also given.

G. W. S.

The Color Value of a Tan Liquor as a Function of the Hydrogen-ion Concentration. By J. A. Wilson and E. J. Kern, *J. Ind. and Eng. Chem.* 13, 1025 (1921). To solutions of gambier and quebracho extract sufficient phosphoric acid was added to bring the p^H value to 2.5. To equal portions of each of these solutions, sodium hydroxide was added to give a series of each ranging in p^H value from 3.0 to 12.0. The gambier series varied in color from light straw at $p^H = 3.0$ to a very deep red at 12.0. The quebracho series was similar in color excepting the liquors having the lower p^H value had a touch of violet. All members of either series appeared practically identical when brought back to $p^H = 3.0$ providing they were not left exposed to the air. A light precipitate formed in all liquors having a p^H value of 4.0 or less. The changes in color of the tan liquors paralleled in a rough way the changes in color imparted to hide.

Liquor exposed to air continued to darken in color the more so the higher their p^H value. Liquors at a p^H value of 9.0 when exposed to the air for a day and then brought back to a p^H value of 3.0 with HCL gave a bulky precipitate. Liquors at a p^H value of less than or more than 9.0 gave a smaller amount of precipitate when subjected to this treatment.

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Between 9.0 and 10.0 the drop in the amount of precipitate is sharp and at $p^H = 10.0$ there is none formed. On the other side of 9.0 the drop is fairly sharp but, nevertheless more gradual. From the fact that the maximum precipitation was obtained with a liquor of $p^H = 9.0$ the authors conclude that this concentration must be a critical point in the oxidation of tan liquors.

G. W. S.

The Tannin Content of Pacific Coast Conifers. By R. H. Clark and H. I. Andrews, *J. Ind. and Eng. Chem.* 13, 1026 (1921). An investigation to determine how the tannin content of western hemlock (*Tsuga heterophilla*) and spruce (*Sitka*) bark varies with the month of the year in which the tree is cut. Samples for nine months of the year were taken from standing or newly felled trees in the region of Kingcome Inlet, B. C. The extractions and analysis were made by the I. A. L. T. C. method. Two separate extractions were made on each sample and the following average results were obtained:—

Month cut	Total solids	Tannin Content: Solubles	Tannin Content: Insolubles	Calculated (Bone Dry): Tannins	Calculated (Bone Dry): Non-tannins
		Western Hemlock			
January 5	18.44	17.78	0.66	12.05	5.73
February 14	20.27	19.64	0.63	13.66	5.98
April 12	22.10	21.66	0.45	14.84	6.82
May 15	22.96	22.28	0.68	15.50	6.78
June 15	22.30	21.70	0.60	15.30	6.40
July 20	20.50	19.16	1.34	14.15	5.01
August 15	15.98	15.48	0.50	11.34	4.14
September 15	14.88	14.57	0.31	10.52	4.05
November 15	12.96	12.89	0.07	9.00	3.89
		Western Spruce			
January 5	18.11	17.23	0.88	12.01	5.22
February 14	24.78	23.64	1.14	14.96	8.68
April 12	26.38	24.89	1.48	17.19	7.70
May 15	26.81	24.60	2.22	16.58	8.02
June 15	24.58	22.72	1.86	15.46	7.25
July 20	24.74	22.72	2.02	15.24	7.48
August 15	22.56	21.09	1.47	15.10	5.99
September 15	22.39	20.79	1.60	16.39	4.40
November 15	27.44	25.30	2.14	17.54	7.76

The average of the nine samples for western hemlock bark is 13 per cent tannin; that for spruce about 15.6 per cent tannin. [Note: The authors do not give anything definite as to the mode of obtaining the nine separate samples.]

G. W. S.

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A Critical Study of Bating. By J. A. Wilson and G Daub, *J. Ind. and Eng. Chem.* 13, 1136 (1921). The examination of more than 200 sections under the microscope failed to reveal any other function of bating than that of the removal of elastin. Therefore this is considered the primary function of bating since the condition of minimum swelling can be obtained by regulating the hydrogen-ion concentration of the solution with which the skin is treated. The paper is confined to the removal of elastin from calfskin and the per cent removed is estimated by microscopical observation of cross sections of samples taken before and after treating. Strips of the sample to be inspected, about 2 in. × 0.5 in., were dehydrated with alcohol and soaked successively in (1) a mixure of equal volumes of alcohol and xylene, (2) a mixture of 1 volume of melted phenol to 3 of xylene, (3) pure xylene, and (4) melted paraffin, after which they were imbedded in paraffin and sectioned at 40 μ The sections were then stained either by means of Weigert's stain or by the following method which was found convenient: The section is washed on a slide with xylene, then with the alcohol-xylene mixture, and finally with pure alcohol. The whole slide is covered with alcohol saturated with Bismarck brown and kept over night in an airtight jar containing alcohol. Next day the section is rinsed with alcohol, alcohol-xylene, phenol-xylene, and finally with pure xylene. A drop of Canada balsam and a cover glass are then put over the section. With a 0.1 gram per liter solution of pancreatin, complete digestion of the elastin was effected only when the p^H value of the solution was between 7.5 and 8.5 but when a 1.0 gram per liter solution was used complete digestion of the elastin was effected between p^H values of 5.5 and 8.5. The temperature was held constant at 40° C. At a constant p^H value of 7.6 complete digestion of elastin was effected by a 1.0 gram per liter solution of pancreatin in 6 to 8 hours; in a 0.1 gram per liter solution not until 24 hours. With the stronger solution digestion started after 2 hours and with the weaker solution not until after 5 hours. Two series were run varying the concentration of pancreatin, one was kept for 5 hours and the other for 24 hours. These showed that complete removal of elastin is effected by 0.1 gram per liter in 24 hours or by 1.1 gram per liter in 5 hours. The effect of the presence of ammonium chlorid in varying amounts in solutions of 0.1 gram and 1.0 gram per liter with a time of digestion of 24 hours was investigated. With the weaker solution it was found that ammonium chlorid in concentrations up to 0.5 gram per liter had an activating effect, while large amounts had a decided inhibitory effect. With a concentration of 0.5 gram per liter of ammonium chlorid 100 per cent of elastin was removed by a solution of 0.1 gram pancreatin in 24 hours while with the same solution containing slightly over 5 grams of ammonium chloride the amount of elastin removed is reduced to zero. Ammonium chloride apparently has no effect on the 1.0 gram per liter solution. An investigation of a commercial bate showed that it had no elastin digesting power which was attributed to its high content of ammonium chloride. Upon

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removal of the ammonium chloride by dialysis the preparation was still without effect. The cause of this is attributed by the authors to the presence of much wood fiber in the preparation.

G. W. S.

Belt Gluing. By U. J. Thuau, *Le Cuir* 10, 350 and 482 (1921). Belt cements may be divided into four classes according to whether the base be: (1) hide or fish glue; (2) rubber or gutta-percha; (3) celluloid, cellulose acetate or nitrate; and (4) mixtures of the above. Of the three usual gelatine glues, *e. g.*, from hides, bones, or rabbit skins, the first is superior in strength because of the elastic fibers of the hide.. For belt glues it is essential to use hide glues and preferable to use only that made from buffalo hides since in these the elastic fibers are the longest. Of the fish glues, that from the intestinal membranes of dried fish is least desirable. The best fish glue is reputed to be obtained from Russia (Solyanski,) but to-day glues of good quality can be obtained from China and Japan. The finest fish glues are generally used in wine clarification. In addition to glues numerous other materials are used such as: whey, denatured alcohol, acetic acid, oil of turpentine, Venice turpentine, garlic, sugar, phenol, glycerine, sandarac and so on. Of these, the use of whey and garlic is empirical.

The use of common garlic bulbs is customary in the manufacture of glues, especially in mixture with flour paste, with which it gives increased adhesiveness and serves even in repairing china. This property of garlic is made use of in belt glues. Whey is used simply for its casein content and the small quantity of free lactic acid present.

With belt glues having a gelatine base, strong joints resistant to both warm and cold water, can be obtained by rendering the gelatine insoluble with such materials as quinone, trioxymethylene, or powdered quebracho extract. The material, reduced to an impalpable powder, is sprinkled on to the laps after applying the glue. Of the above three materials quinone gives the best results. The quantity required is so small that the increase in cost is not material.

The following formulas for belt glues are given:—

Formula No. 1: Whey—15 liters; garlic—4 strings (?); fish glue (Saigon)— 1.5 kgs. The mixture is boiled on a steam bath for 8 hours, then expressed, filtered, and again heated with 4.5 kgs. of hide glue, previously soaked for 10 hours with a little of the whey. Complete solution requires about 1½ hours; it is then removed from the steam bath and when cooled to 50°—60° C., 2 liters of 90° denatured alcohol are added. It is then stirred for 10 minutes and run into molds or plates. This formula has been used with satisfaction for about 50 years. It might be criticised as being empirical in the use of garlic and whey and it is suggested that the addition of a little acetic acid would be an improvement.

Formula No. 2: 500 gms. of hide glue, 120 gms. of gum arabic, and 120 gms. of fish glue are soaked overnight in water, boiled until completely

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dissolved, then 20 gms. of alcohol, 10 gms. of Venice turpentine and 10 gms. of oil of turpentine are added.

Formula No. 3: 5 kgs. of hide glue are soaked in cold water for 8 or 10 hours and then heated on a steam bath with constant stirring until the mass becomes clear and the excess of water evaporated off; 3.75 liters of acetic ether previously warmed are next added and after agitating thoroughly 5 gms. of pulverized alum, 20 gms. of shellac in a 1 to 10 solution of ethyl or denatured alcohol 90° Bé, and 1 gm. of potassium chromate in a 1 to 10 solution of warm acetic ether are added. The entire mixture is boiled then for an hour.

Formula No. 4: 1 kg. of Cologne glue is dissolved in 1.5 liters of warm water, evaporated to a syrup and mixed with a warm mass of 100 gms. of turpentine and 5 gms. of phenol. After cooling the opaque mass is cut into small cubes and dried. In about 2 days it is ready for use by dissolving in vinegar or acetic acid, and is applied warm (30°—40° C.) under pressure.

Formula No. 5: 50 gms. fish glue; 100 gms. hide glue; 150 gms. whey; 50 gms. 90° alcohol; 50 gms. acetic acid; 50 gms. garlic; and 50 gms. sugar. The fish glue is swollen with ⅓ of the whey, the acetic acid or vinegar and powdered garlic added and the mixture melted on the steam bath. The hide glue is melted separately with the rest of the whey, mixed with the fish glue, the alcohol and sugar added and the entire mixture allowed to simmer on the steam bath for a day. To preserve the glue, add while liquid 20 gms. of boric acid or 5 gms. of salicylic acid.

Formula No. 6: 100 parts of hide glue are softened in water. The excess water is poured off, the glue melted and 2 parts of glycerine and 3 parts of potassium dichromate added. This is applied warm.

Formula No. 7: 1 kg. of hide glue is dissolved in 1.3 liters of warm water and thickened to a syrup; 100 gms. of Venice turpentine and 5 gms. of phenol are mixed with it, and the whole is dried for 2 days. It is moistened with a little vinegar or acetic acid before using.

Formula No. 8: 250 parts of rabbit skin glue, 60 parts of fish glue and 60 parts of gum arabic are heated with water until a uniform solution is obtained; 5 parts of Venice turpentine, 6 parts of oil of turpentine, and 10 parts of 90° denatured alcohol are then added.

Formula No. 9: 6 parts of sandarac in 100 parts of 90° denatured alcohol and 6 parts of oil of turpentine are heated to boiling and mixed with an equal volume of fish glue dissolved in warm water to the consistency of a paste. This formula should be warmed before applying.

Formula No. 10: 4 kgs. of buffalo hide are boiled with 20 liters of water for 5 hrs., strained, and 800 gms. of fish glue and 8 liters of whey added. This is again heated until solution occurs and 8 kgs. of hide glue, previously soaked overnight, are added. When this has dissolved, the solution is cooled to 50° C. and 250 gms. of acetic acid and 1 liter of 90° denatured alcohol are added with thorough stirring. The whey can be replaced by 250 gms. of ammonia casein.

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From the above formulas it should be possible, by experimenting, to choose a satisfactory one or to develop one. Formulas No. 1 and No. 10 are preferred, especially with the use of quinone to render the joints waterproof. If these formulas do not give a sufficiently flexible glue, it can be remedied by adding a little glycerine.

Belt cements with a base of caoutchouc or gutta-percha. Success with cements of this kind depends primarily upon the method of application. It is essential that the surface to be cemented be clean, then warmed, spread separately with the cement and then reheated to melt the cement, when they should be quickly pressed together and maintained, for at least 24 hrs., under heavy pressure. The following formulas are given:

Formula No. 1, Digest 30 gms. of good rubber at 30° C. with 180 gms. of carbon bisulphide; to prevent undue thickening add from time to time with constant stirring part of a solution containing 60 gms. of turpentine, 15 gms. of rubber and 8 gms. of rosin.

Formula No. 2. A very simple formula consists of rubber dissolved in benzene to the consistency of honey.

Formula No. 3. A solution of the consistency of honey made by dissolving gutta-percha in chloroform. This formula is very successfully used in America for patching shoe uppers.

Formula No. 4. Mix 4 parts of carbon bisulphide with 1 part caoutchouc and ½ part gutta-percha and let stand in a closed flask for 10 hrs.

Formula No. 5. A very adhesive cement is made from 6 parts of amyl acetate and 1 part of pure Para rubber. The mixture should stand about a week before using.

Formula No. 6. Heat 1 part of rubber with 12 parts of mineral or coal tar naphtha, and add 20 parts of gum lac. The mixture is poured on a slab to cool and reheated to 120° C. when ready to use.

Formula No. 7. Mix 10 parts of carbon bisulphide and 1 part of turpentine with sufficient rubber to give a soft mass.

Formula No. 8. Mix a solution of 100 gms. of carbon bisulphide and 15 gms. of rubber with one containing 10 gms. of turpentine and 10 gms. of gum lac.

Formula No. 9. Dissolve 10 gms. of asphaltum, 10 gms. of rosin and 40 gms. of gutta percha in 200 gms. of carbon bisulphide.

Formula No. 10. Dissolve 5 gms. of rubber in 100 gms. carbon bisulphide and add to this viscous mass, with thorough stirring, 5 gms. of sulphur chloride.

Belt cements with a base of celluloid, cellulose acetate or nitrate. — Cements of this type are becoming more and more popular in belt cementing and for use with light shoes and small leather articles. Because of their inflammability cellulose acetate cements are more generally used

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Formula No. 1. Dissolve 15 parts of cellulose acetate in 100 parts of amyl acetate or acetone, a few gms. of castor oil may be added to increase flexibility.

Formula No. 2. Dissolve 15 parts of cellulose acetate in a mixture of 90 parts of tetrachloro-ethane and 10 parts of 90° alcohol.

Formula No. 3. Dissolve 15 parts of cellulose nitrate or gun cotton in 95 parts of amyl acetate or in 90 parts of acetone mixed with 10 parts methyl alcohol. Acetic acid or benzene can be added according to results desired. For increased flexibility castor oil can be added. The cellulose nitrate can be replaced by celluloid.

Mixed cements.— A great variety of formulas can be obtained by mixtures of different types of cements as shown by the following examples.

Formula No. 1. Mix 1 part of powdered gum lac with 10 parts of ammonia; the transparent mass becomes liquid after some time, 3 or 4 weeks. Rubber in contact with this mixture becomes soft and dissolves and when the ammonia evaporates the rubber hardens and becomes adhesive. Casein can be substituted for the gum lac.

Formula No. 2. Dissolve considerable cellulose nitrate in a mixture of 55 per cent amyl acetate, 12 per cent fusel oil; 10 per cent acetone and 23 per cent benzene; add a solution of rubber in carbon bisulphide.

Formula No. 3. Cyclohexanone substituted in some of the preceding formulas gives cements of extraordinary strength.

R. W. F.

The Basicity of Chromium Salts and their Graphical Presentation. By G. Grasser, *Coll.* **615**, 319-25 (1921). Basicity may be plotted against tanning intensity as is shown in Fig. 1. Chromic sulfate $Cr_2(SO_4)_3$ is completely soluble and ionized and therefore has a colloidal condition of zero. Zero is again reached with chromic hydroxide, $Cr_2(OH)_6$ or (Cr_2O_3 + 3 H_2O) which is insoluble. The curve begins in the zone of true solution, reaches the colloidal zone at z, and then at y passes over to the zone of the insoluble salts. The negative portion of the curve, *i. e.*, the portion below the axis of abscissas, lies in the zone in which the chromium is in the oxide condition. At the point of maximum tanning intensity, y, the acidity is equal to the basicity and neutrality has been reached as is shown by the formula, $Cr_4(SO_4)_3(OH)_6$. The basicity expressed by Schorlemmer's method (see Abstract, this Jour. **16**, 284 (1921.) may be represented as shown in Fig. II. The number of SO_4 groups is plotted as ordinates and the basicity as abscissas. The lower curve represents the composition of salts having two, and the upper curve that of salts having four chromium atoms per molecule. The number of OH groups in any compound is twice the difference between the ordinate for the compound and the point where the curve cuts the SO_4 axis.

I. D. C.

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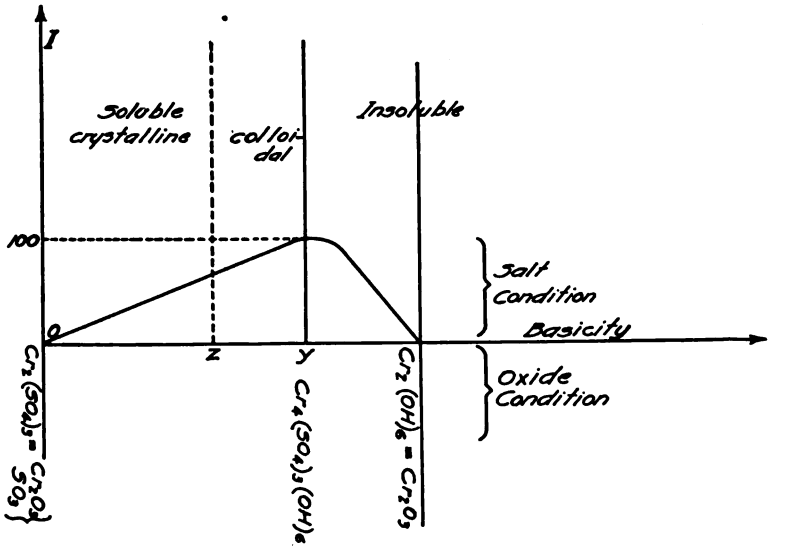

Figure I

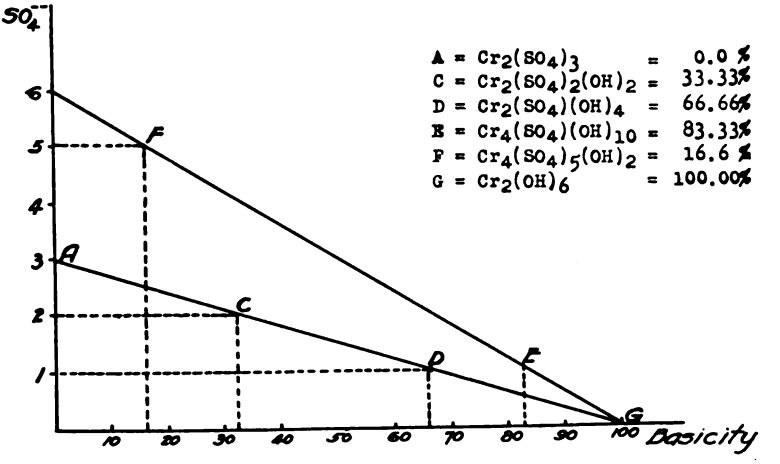

Figure II

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Cinchonine in the Qualitative and Quantative Determination of Sulfite-cellulose. By L. De Hesselle. *Coll.* **618**, 425–30 (1921). Appelius and Schmidt (See This Journal **9**, 566; **10**, 64 and 202) found that cinchonine or cinchonine sulfate solutions gave a flocculent precipitate with tannin which dissolved on boiling while sulfite-cellulose gave a lumpy precipitate which did not dissolve on boiling. De Hesselle's modification of their method is as follows. *Solutions required.* (1) fifteen g. pure cinchinone is mixed with 100 cc. of water, conc. sulfuric acid is added until the cinchonine dissolves then the solution is made up to one liter, (2) 15 g. purest tannin is dissolved in a little hot water, cooled and made up to one liter, (3) 40 per cent hydrochloric acid. *Qualitative test.* One hundred cc. of the solution of analytical strength is boiled for 2 min. with 5 cc. of hydrochloric acid (40 per cent,) then cooled and filtered. Fifty cc. of the filtrate, which must be absolutely clear, is mixed with 10 cc. of the tannin solution and 10 cc. of the cinchonine solution and slowly heated to boiling. If sulfite cellulose is present a dark brown lumpy precipitate will remain. *Quantitative test.* Seven and five tenths g. of sulfite-cellulose is dissolved in 450 cc. of hot water, 25 cc. of 40 per cent hydrochloric acid is added and the solution made up to 500 cc. One hundred cc. of this solution is boiled 2 min., cooled, made up to 100 cc. and filtered. To 50 cc of this solution (absolutely clear) is added 10 cc. each of the tannin and the cinchonine solutions and the mixture is heated slowly to boiling. It is then filtered hot through a weighed filter, washed 2–3 times with hot water, and dried first for 2 hours at 100° then for half hour periods to constant weight. One gram of the precipitate is equivalent to 1.35 grams of sulfite-cellulose extract (dry,) or to 2.74 grams of extract containing 50 per cent water. Results given by the author vary from 1.47 to 1.18 (ave. 1.35) and from 3.05 to 2.37 (ave. 2.74.) Synthetic tannins react partially like the vegetable tannins, others like sulfite-cellulose, while others do not give the reaction at all. There is however a difference in form and appearance between the precipitates with sulfite-cellulose and synthetic tannins with the exception of Ordoval G and 2G which will be treated in a later article. I. D. C.

The Action of Acids Containing Arsenic in the Reducing-bath of the Two-bath Chrome Process. By K. Schorlemmer, *Coll.* **618**, 430–35 (1921). The fact that the usual quantity of hydrochloric acid used in the reducing bath with thiosulfate was insufficient if the acid contained arsenic was observed by the author about 20 years ago and later also by Stiasny (Coll. 1912 p 461) and Raschig (*Zeit. Angew. Chemie* **88**, 260 (1920.)) Sulfurous acid and free sulfur are formed when acid is added to a thiosulfate solution (Eq. 1;) also one atom of iodine oxidizes one molecule of thiosulfate (Eq. 2) and only one-half of one molecule of sulfurous acid (Eq. 3.)

(1.) $Na_2S_2O_3 + 2HCl \longrightarrow H_2SO_3 + S + 2NaCl$

(2.) $2Na_2S_2O_3 + 2I \longrightarrow Na_2S_4O_6 + 2NaI$

(3.) $H_2SO_3 + 2I + H_2O \longrightarrow H_2SO_4 + 2HI$

(4.) $5Na_2S_2O_3 + 6HCl \longrightarrow 2Na_2S_5O_6 + 6NaCl + 3H_2O$

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Therefore an acidified thiosulfate solution should reduce twice as much iodine as an untreated solution. However not over 1.6 or 1.7 times as much iodine is ever reduced, for part of the thiosulfate is always changed to polythionates which do not reduce iodine. In the presence of arsenic Raschig found that very little sulfurous acid was formed, almost all of the thiosulfate being changed to pentathionate (Eq. 4,) which has no reducing action. The maximum quanity of arsenic which might be present without influencing the reduction was determined by adding 3 cc. of C. P. hydrochloric acid and varying amounts of sodium arsenite to 10 cc. portions of N/10 thiosulfate diluted with 50 cc. of water and titrating with iodine after the mixtures had stood for 3, 13 or 23 minutes. The results, omitting duplicates, were as follows,

	Cc. N/10 iodine		
10 cc. N/10 thiosulfate and—	3 min.	13 min.	23 min.
no acid	10.11	10.11	10.11
3 cc. acid	10.8	11.37	11.80
3 cc. acid and 3 mg. arsenic	9.94	7.96	6.5
3 cc. acid and 1 mg. arsenic	10.1	8.95	7.8
3 cc. acid and 0.5 mg. arsenic	—	—	8.4
3 cc. acid and 0.3 mg. arsenic	—	—	9.66
3 cc. acid and 0.1 mg. arsenic	—	—	11.4
3 cc. acid and 0.05 mg. arsenic	—	—	12.2

The acid should thus not contain more than 0.1 mg. sodium arsenite in 3 cc. or 0.0015 per cent As_2O_3. If much arsenic is present it will be adsorbed as the sulfide and will appear in the finished leather.

The time of action, the concentration of the solution, the quantity and kind of acid, and the temperature also influence the above reaction (Eq.1) but their influence was not investigated.

I. D. C.

The Tannin of the Native Oak. By E. VOLLBRECHT, *Coll.* **617**, 394–401 and **618**, 418–25 (1921). The first real progress in the determination of the structure of the tannins was made by Fischer when he identified the group of ester tannins. These have as the acid component gallic or caffeic acids and as the alcoholic component, sugars, quinic acid or gallic acid. They occur with glucosides of ellagic acid and these together form the group of hydrolysable tannins. The condensed tannins, on the other hand, are very difficult to break up and of this group only the catechins have been investigated. They resemble the flavones, flavonones and anthocyanidines and have in one ring resorcin or its oxidation products phloroglucine or oxyphloroglucine and in the other ring a hydroxyl arrangement as in p-oxybenzoic, protocatechuic, or gallic acids. Tannins intermediate between the ester and condensed classes also occur. Previous work on oak tannin has been principally on tannin obtained from *Quercus pedunculata* and *sessiliflora*. Strongly colored extracts were used and purified by rejecting the ether soluble, the water insoluble and the more highly

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colored fractions from fractional precipitation so that the purified tannin was a small fraction of the total. Disagreement in results is therefore due to unsuitable preparation as well as to differences in the tannin itself. Previous results show that a small amount of ellagic acid and probably less than 1 per cent sugar is present while little or no gallic acid is present in the leaves, wood or bark.. Grabowski found that phloroglucin, protocatechuic acid and pyrocatechin were produced by fusion of the tannin with potassium hydroxide but this has never been confirmed. Most of the tannin is an unidentified colored mass more or less soluble and which easily changes to "oak red."

The tannin for the present work was prepared as follows. Young shoots of *Q. pedunculata* were gathered in May and before they had wilted, and therefore before the plant enzymes had acted on the tannin. they were extracted for ten min. with boiling water. The extraction was repeated 2-3 times and the combined extract precipitated twice with lead acetate and decomposed with dilute sulfuric acid. A small amount of lead acetate was again added and the solution filtered,, treated with hydrogen sulfide, concentrated, extracted 24 hours with ether, then concentrated at low pressure and dried in a dessicator. A dark green residue containing most of the mineral matter remained after dissolving the tannin in alcohol. Three times the volume of ether was added to the alcoholic solution then the solution was filtered and evaporated under reduced pressure. Water was added and evaporated to remove the organic solvent then the tannin was dried in a dessicator. Two hundred and seventy-five grams of tannin were obtained from 20 kilograms of shoots. This was 75 per cent of the total tannin and no important constituent had been lost. This "raw tannin" was a dark reddish-brown mass, easily soluble in water giving a strongly acid solution, and containing about one-fourth of its weight of bound ellagic acid, and several per cent of mineral matter. It was soluble in alcohol of every concentration, in methyl alcohol and acetone, only slightly soluble in acetic ether and not at all soluble in ether.

Attempts to separate the tannin into its components by fractional precipitation first with lead acetate then from an alcoholic solution with ether were not successful. On heating for 20 hours at 100° with 3 per cent sulfuric acid, ellagic acid and about 6 per cent of sugar, mainly glucose, were split off. The first 10 per cent or 15 per cent of ellagic acid was given off readily, the remainder very slowly so this acid may not all be bound in the same way. The remainder of the tannin was changed to a dark carbonaceous mass. Dilute sodium hydroxide caused the separation of 27 per cent of ellagic acid which must therefore be bound as an ester.

A slow hydrolysis of the tannin was produced by tannase and by *aspergillus niger*. The latter was however much better than the former. In the tannin, after complete hydrolysis by tannase, it was possible to separate and identify about 25 per cent ellagic acid, 4-6 per cent quercitin, 6 per cent sugar, a trace of gallic acid and 50 per cent of a basic or fundamental tannin. This fundamental tannin had a strong yellow color,

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contained about one per cent mineral matter, 50.8 per cent carbon and 3.6 per cent hydrogen. It gave a heavy precipitate with gelatine, a blue-black coloration with iron salts and was optically inactive if the quercitin compound, which causes a laevorotation, had been completely removed. Since one gram requires 26 cc. of N/10 sodium hydroxide for neutralization the molecular weight may be either 385 or 770 if it contains 1 or 2 carboxyls. It was changed to a dark decomposition product by dilute alkali or hot acid. It was soluble in water and alcohol, less soluble in acetone scarcely soluble in acetic ether and insoluble in ether. No phloroglucine was produced by fusion with potassium hydroxide and no other products could be separated from or identified in the fused mass. This tannin, since it belongs to the condensed tannins but not in the catechine class, is a member of an entirely new class.

The results, in general, show that the tannin of the oak leaf is accompanied by free ellagic acid and a substance which contains combined quercitin. This latter substance is decomposed by acid but not by dilute alkali and, since sugar is also set free with the quercetin in about the correct proportion, it may be a diglucoside of quercitin. Ellagic acid and the fundamental tannin are probably combined as an ester and in the proportion of one molecular weight of acid to 760 grams of the tannin.

The tannin from the leaves and leaf galls of *Quercus sessiliflora* and from galls from *Q. pedunculata* was apparently identical with the above described tannin. The fundamental tannin of Spanish chestnut wood (*castanea vesca*) is also the same although this tannin contains some gallic acid and more of the decomposition product and of the quercitin compound.

I. D. C.

The Tanning Process in the Presence of Alkali. Contribution to the Theory of Tanning. By W. Moeller. *Zeitschrift für Leder-und Gerberei-Chemie.* 1, 2 (1921). The action of quebracho tannin on hide powder in the presence of increasing amounts of sodium hydroxide was investigated and it was found that the absorption of tannin in the presence of alkali under the conditions used was practically nil while hydrolysis predominated. The procedure used was similar to that employed by the author in preceding work on the processes of tanning. In this case a 6 per cent solution of quebracho was used containing amounts of sodium hydroxide giving concentrations of N/100, N/10 and N/1. In the theoretical discussion the author deprecates the prevailing teachings in explanation of the tanning processes, that leather formation is due to a union of oppositely charged bodies, the hide molecule being positive and the tannin particle negative. Such a theory really only explains the cause of the force which leads to mutual attraction and the release of the tanning process, but it does not explain the most essential facts that then the hide molecules resist hydrolytic and fermentative influences. It is easy to experimentally demonstrate that protein bodies mutually precipitated are in no way resistant to these influences. The author calls attention to recent physical and colloid

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chemical work; especially of Bethe and Keller on the determination of the charge of colloids. Walden [*Zeitsch. für phys. Chem.* **94**, 263 (1920)] has shown that the undissociated portion of the molecules alone, without the help of the dissociated molecules can influence electrical processes. Until lately the opinion prevailed that not only chemical but also most of the physical actions were only to be explained by the dissociated molecule. Keller [*Zeitsch für phys. Chem.* **98**, 338 (1921)] has definitely pointed out that most dyes as well as some other substances, some of which are used in tanning, as, ferric hydroxide sol, are subject to a change in their electric charge. He states that non-dissociated and associated bodies are no longer acid or basic but must be regarded as neutral. These neutral bodies in an acid dispersion medium appear relatively positive and migrate to the cathode and in a basic solution the reverse. He also considers the various hypotheses according to which it owes its charge to the adsorption of H or OH ions as unnecessary. The assumption that the dielectric-constant is of exclusive importance for the kind of charge and the direction of migration appears much more justifiable, especially in adsorption experiments. It is probable that colloidal tannin particles in acid solution have a positive charge.

In connection with the experiments which form the subject of this paper the author states that he has repeatedly emphasized that a certain decomposition of the hide substance is necessary for the progress and accomplishment of tanning, merely by opening up a sufficiently large surface of the micellar-complexes. It makes no difference whether this is accomplished with acid or alkali. In this point only is the nature of the charge important. Acid hydrolysis must come to a standstill since the liberated valencies of the cleavage products combine with acid and eliminate it for further hydrolysis. The relations are entirely otherwise in alkali hydrolysis. The electric charge and direction of migration of the liberated hide substance remain continually the same even in dilute solutions. The same case will obtain in acid hydrolysis with a definite excess of hydrogen ion, as soon as the acid addition is sufficient to continue to hydrolyze and to bind the liberated valencies during the whole process.

G. W. S.

The Hydrolytic Action of Neutral Salts on Hide, I. By W. Moeller, *Zeitsch. für Leder-und Gerb. Chem.* **1**, 12 (9121). Quantitative experiments were conducted as in previous work with hide powder and solutions of sodium chloride, sodium sulfate, ammonium sulfate and ammonium bisulfate at several concentrations and for several different periods of time.. The author concludes that the hydrolytic action of sodium chloride solutions up to 15 per cent strength is independent of the concentration and dependent on the time. At the end of a time period of 4 weeks there was found about 12 per cent of hide substance in solution. Up to 14 days there is no noteworthy hydrolysis to be observed. Sodium sulfate hydrolyzes with greater regularity reversely proportional to the concentration and directly proportional to the time of action. With sodium sulfate

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solution, at a strength of 15 per cent, hydrolysis is practically nil. Ammonium sulfate hydrolyzes in solutions of 1-5 per cent strength independently of the concentration and in small measure dependent on the time. With acid ammonium sulfate solutions the hydrolysis is directly proportional to the time of action and in small measure is dependent on the concentration.

G. W. S.

The Processes in the Oiling of Leather. By W. Moeller, *Zeitsch. für Leder-und Gerg. Chem.* **1**, 20 (1921). Since Knapp's time it has been known that the train oil which is incorporated in leather cannot be quantitatively removed again with a fat solvent. From this it has been concluded that either the oil has undergone a chemical change, rendering a part of it insoluble, or that it is partly retained by the leather in a physical manner. Knapp assumed that it was a retannage of finished leather with train oil and considered bark tanned upper leather as a combination of bark tanned and chamois tanned leather. The author considers that such a view would lead to the assumption that bark tanned leather itself is untanned and that the collagen either, according to the chemical theory still possesses free valencies or, according to the physical theory, still possesses free surface. It has not been clear in what manner the change in the train oils occurred. Whether it was through contract with the oxygen of the air or through contract with the tannin in the leather, with the leather itself or the hide which it contained. The work upon which this paper is based is for the purpose of explaining this, at least in part. Forty gram portions of train oil were stirred into one hundred and sixty grams each of liquid oak bark, chestnut wood, oak wood, quebracho, mangrove bark, pine bark, mimosa bark, myrobalan extracts and a 45 per cent solution of technically pure tannin. The mixtures were allowed to stand 3 days, stirring several times daily. A measured amount of the mixture was then brought to dryness on the water bath, and the residue extracted successively with petroleum ether, ethyl ether and hot water. The fat constants of the petroleum ether soluble were determined for comparison with the original oil. The results were as follows:—

	Petrol. ether Soluble	Ethyl ether Soluble	Acid value	Analysis of Petrol. Ether Soluble					
				Sap. value	Iodine value	Neutral fat	Unsap.	Fatty acids	Oxy-fatty acids
Oak Bark	17.7	3.0	62.7	208.9	98.7	77.5	1.1	66.6	20.2
Mimosa Bark	20.2	0.6	77.1	236.2	94.1	67.2	1.4	71.0	20.2
Pine Bark	19.1	1.9	57.9	222.2	66.9	73.8	1.0	65.9	19.0
Quebracho Wood	20.5	1.0	54.3	193.6	79.5	68.7	0.9	64.8	20.0
Mangrove Bark	31.3	0.9	58.1	200.8	96.9	70.0	1.2	79.8	21.0
Ook Wood	20.5	0.9	53.7	169.1	85.9	68.2	0.9	70.0	13.1
Chestnut Wood	18.4	1.4	48.8	249.2	63.1	77.7	1.0	58.7	20.0
Myrobalans	21.0	2.7	49.9	185.1	81.3	73.3	0.9	64.7	18.6
Tannin	24.6	1.0	65.2	199.7	125.8	67.4	0.4	84.1	9.0
Pure Train Oil	100.0		59.4	187.2	139.6	68.2	0.7	87.8	2.5

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The author gives his theory of the mechanism of the formation of the oxidized fat and also his views of the functions of leather oils which have been given before (see Abst. This JOUR. **15**, 176, 1921).

G. W. S.

The Proteolytic Constant in Vegetable Tannage. BY W. MOELLER, *Zeitsch. für Leder-und Gerb. Chem.* **1**, 28 (1921). In this paper are given the results of a continuation of the investigation of the action of tannin and quebracho solutions on hide powder extended to a time period of 6 months. [See Abst., This JOUR. **16**, 223 (1921).] The experiments were conducted with one hundred cc. of 10, 20 and 30 per cent solutions and one thousand cc. of 1, 3 and 5 per cent solutions with 4.4 gram portions of hide powder. The author concludes that the absorption of tannin (technically pure) by hide powder is independent of the concentration and the volume and exclusively dependent on the absolute amount of tannin presented. A so-called case-hardening does not occur with tannin even in extreme concentrations. However, concentrated quebracho-tannin solution does effect case hardening which begins at a solution strength of about 6 to 10 per cent quebracho. The proteolytic constant, or the per cent of hide substance removed from the hide powder, remains unchanged in all concentrations and in unlimited time periods.

G. W. S.

Valonea. ANON, *Gerber*, **47**, 113 (1921). Valonea are the fruit of several species of oak which grow wild in Asia Minor, in the Balkans, and in Greece and its island possessions. *Quercus Valonea* is indigenous to Asia Minor and its fruit has broad, angular scales on the cup. *Quercus macropolis* is the Greek oak and its fruit has flat scales on the cups. The valonea are gathered when they are ripe by picking or knocking from the trees with sticks and are dried on the ground before being transported. Valonea are of two general kinds:—(1) Smyrna—which come from Asia Minor and contiguous islands. They are larger, richer in tannin, and of lighter color and are therefore much preferred. (2) Greek—from the Balkan peninsular and Grecian islands. These are smaller, darker and have less tannin and therefore are cheaper. Smyrna valonea is sorted into four grades:—(1) Smyrna valonea, first class, also fines, mezzana, tribleé or Uso Trieste. Consists of large, light colored cups almost without acorns. (2) Prime Smyrna valonea, or Unagna. Consists of large and small cups with few acorns. (3) Seconds, also Inglese or Uso Anglais. Consists of medium and small, darker cups with a good many acorns. (4) Refuse, Refuso or Scart. Consists mostly of damaged or small cups of bad appearance with many acorns.

The scales of the cup commonly known as the beard or "trillo" contain the most tannin, the cups less and the acorn least. According to Paessler, the whole valonea consists of about 50 part cups, 30 parts beard or scales and 20 parts acorn and the average tannin content of each is about as follows:—Cups 24.5 per cent; beards, 45.0 per cent; acorn, 15 per cent. The

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tannin content of valonea varies considerably and although, in general, the Greek valonea has a lower content than Smyrna when they are typical, it is not always true. Moreover names of valonea cannot be accepted as guarantee of their authenticity or as a criterion of their tannin content. Therefore they should only be bought on analysis.

Valonea extract, manufactured in Smyrna, appears in commerce in liquid and solid form under the name of Valex and Velonitan. These extracts are easily soluble even in cold water but a temperature of 30° to 40° C. is the best.

In the use of valonea, it must be remembered that its tannin is one of the best which we possess and that its price is proportionately high. Therefore it should be used as oak bark only for the production of better kinds of leather. Valonea gives a tough and firm leather and is of first importance for sole, side and belting leather. In general it is not used for saddlery or upper leather. It gives a light color and dark cut to the leather which is valued so much for bottom leather and it deposits a white coating, "bloom," principally on the grain side which is considered as the mark of an especially good tannage. The inferior kinds of valonea and also the beard, are leached alone and also in mixture with other materials, and this extract is used for the handlers and for filling the tan pits and lay-aways. It is also used, as well as the better sorts, in the crushed form for the layers. If valonea is used in large quantity the hide is first covered with ground bark and then with ground valonea on top of which another layer of ground bark is placed before the next hide is put in. When ground valonea comes in direct contact with the hide, uneven tannage and the formation of spots occur. When valonea is used in small quantity it is thoroughly mixed with the other materials before being used in the tan pack. Valonea is only used alone in exceptional cases, in general it is used with pine or oak bark in order to raise their tannin content. Thus increasing the strength of the liquor, shortening the time of tannage and increasing the weight of leather. Valonea should not be ground too fine for leaching as it will give trouble. Still it should not be leached without grinding as Parker has shown that two-thirds of the tannin content may be lost in this way. Valonea can be substituted in part by cheaper materials, as knoppern, myrobalans, and divi-divi, but the complete action of the valonea will not be obtained. Valonea should be used in the last layers and the substitutes in the preceding ones. Oak and chestnut wood extracts are well suited for this. In the countries of the former Austria-Hungary valonea in combination with knoppern and myrobalans was much used, especially for the so called "Terzen" tannage.

G. W. S.

PATENTS

Material Resembling Leather. U .S. Patent 1,382,947. D. BEATTY, Berkeley, Calif. Filed Oct. 8, 1917. A leather substitute comprising coagulated, pliable and moisture-resistant viscose containing fiber therein.

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Method for Finishing Leather. U. S. Patent 1, 385,184. W. H. MEADE and and S. H. FRIESTEDT, Camden, N. J. Filed Oct. 14, 1919. As a new article of manufacture, leather having a coating including selenium.

Readily-Soluble Tanning Agent. U. S. Patent 1,390,205. F. HASSLER, Hamburg, Germany. Filed July 9, 1920. As a new article of manufacture, readily soluble tanning extracts, comprising a natural tan and a sulfonic acid of an at least tricyclic hydrocarbon.

Tanning. U. S. Patent 1,390,735. J. K. TULLIS, New York, N. Y., Filed Sept. 24, 1918. Comprises treating a hide with a solution of bichromate containing aluminum sulfate and magnesium sulfate, and then effecting reduction in the hide and tanning by treating with a sulfite waste liquor material.

Stretcher and Drier for Hides and Leather. U. S. Patent 1,392,968. J. ROBINSON, Aurora, Ontario, Canada. Filed Dec. 8, 1920.

Color-Base for Leather-Finishes and Method of Making the Same. U. S. Patent 1,393,697. J. H. PFINGSTEN, Milwaukee, Wis. Filed May 28, 1921. A concentrated color base suitable for making leather finishes, which consists of a finely ground pigment, water soluble oil, and water, and containing a small amount of mercuric chlorid.

Process of Making a Depilatory for Hides and Skins. U. S. Patent 1,394,588. A. H. STONE, Boston, Mass. Filed May 23, 1919. In the process of making a depilatory from lime and sodium sulfid liquor the improved step which consists in a prolonged agitation while hot of the result or product of the reaction of said ingredients, whereby the depilatory is obtained in solid form and latitude in the character of the ingredients used is afforded.

Tanning. U. S. Patent 1,395,733. A. RÖMER, Stuttgart, Germany, assignor, by mesne assignments, to The Chemical Foundation, Inc., a Corporation of Delaware. Filed Dec. 23, 1916. The process of tanning which comprises treating the skins in a bath containing formaldehyde and subsequently in a bath containing a soluble aromatic compound containing an amino group and capable of forming an insoluble product with formaldehyde.

Leather-Preserver. U. S. Patent 1,398,600. H. A. MUTHS, Mobile, Ala. Filed May 25, 1920. A composiion comprising a mixture of castor oil, paraffin, Venetian turpentine, and oil of cinnamon.

Process of Making Tanning Materials. U. S. Patent 1,399,510. W. MOELLER, Hamburg, Germany, assignor, by mesne assignments, to The Chemical Foundation, Inc., a Corporation of Delaware. Filed Mar. 14, 1916. The preparation of a tanning agent which comprises condensing a derivative of an aromatic hydro-carbon to an insoluble condensation product, and subsequently oxidizing said condensation product until a substantially water soluble material is obtained.

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Leather Working Machines. British Patent 165,791. C. RAUSCH, Dresden, Germany. July 4, 1921, No. 18074. Machine for boarding, breaking and staking.

Leather-Working Machines. British Patent 166,126. D. MERCIER, Annonay, Ardéche, France. July 1, 1921, No. 17922.

Treating Hides, Etc. British Patent 166,495. A. MANVERS, London Feb. 14, 1920. In preparing hides for tanning, they are suspended in an autoclave provided with pipes for obtaining a high vacuum, for filling and emptying and cocks for admitting air when required. In the case of hard salted hides, they are subjected to vacuum to exhaust occluded air and are then softened in water under vacuum, blasts of air being admitted through the cocks from time to time, to agitate the water and dash the hides about. Hides are limed in a similar manner, lime and water with or without other chemicals being introduced and the temperature raised to about 80° F., the vacuum being maintained and occasional blasts of air admitted to stir up the lime. The hides are subsequently washed, delimed with a little acid and, if not to be immediately tanned, are dried in a partial vacuum with hot air.

Splitting or Skiving Leather, Etc. British Patent 166,699. S. SOKAL, London.—April 20, 1920, No. 10988. Relates to band-knife machines for splitting or skiving leather, etc.

Tanning. British Patent 167,538. W. H. OCKLESTON, CHESTER, KELSALL, and T. B. CARMICHAEL, Waterloo, near Liverpool. April 30, 1920, No. 119699. In tanning processes in which starch is employed to increase the efficacy of the tanning liquor, ordinary starch is preparatorily treated to render it soluble, being then added to the tanning-liquor and treated therewith. Known methods for producing "soluble" starch may be employed.

Tanning. British Patent 167,771. V. PERADOTTO, Turin. Aug. 10, 1921. No. 21298. Tanning liquor is circulated rapidly in a tank or vat by a screw or paddle, the vat being divided by a central partition.

Tanning. British Patent 167,785. A. MANVERS, London. Feb. 14, 1920, No. 4557. Hides preferably after being subjected to a high vacuum, are tanned under pressure by liquor from which all air has been removed. Treatment with thin glue or gelatine may follow. The depilated and preferably dried hides are suspended in an autoclave and subjected for 30 to 60 minutes to a high vacuum, a strong tanning-liquor from which all air has been removed by passage through a vacuum machine, etc., being then pumped in, preferably under a pressure of from 20 to 40 lb. per sq. in. After the tanning-liquor has been run off, the hides are washed, and a solution of thin glue or gelatine is forced into the pores by alternate high vacuum and high pressure. The hides may be again washed and are dried *in vacuo*, small quantities of hot air being admitted, preferably through a red-hot pipe.

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Annable, C. H., % Donnell Carman, Mudge, Inc., New Toronto Ontario, Canada.

Frank, E. H., % Linden Tanning Co., Newark, N. J.

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Fisher, W. R., % A. C. Lawrence Leather Co., 161 South Street, Boston, Mass.

Haffner, Edwin, % The Haffner Bros. Co., Cincinnati, Ohio.

Limmer, Harry, % Richard Young Co., 488 Morgan Avenue, Brooklyn, N. Y.

Ross, B. C., % A. H. Ross & Sons, 1229-37 North Branch St., Chicago, Illinois.

CHANGES OF ADDRESS

Bacon, C. B., 864 Nostrand Avenue, Brooklyn, N. Y.

Harrington, T., % Monarch Leather Co., W. Division Street, Chicago, Illinois.

Kidston, Filmer, Chromepet P. O., near Madras, India.

ADOPTION OF PROVISIONAL METHOD

The following method for the Determination of Free Sulphuric Acid in Leather has been voted by the Association as a provisional method:

Determination of Free Sulphuric Acid in Leather

Weigh a 2 gram sample. Add 25 cc. of N/10 sodium carbonate in the case of an unloaded leather (or a larger amount, 35 or 50 cc. in the case of a leather highly loaded with Epsom salts). After careful evaporation to dryness ignite the contents of the dish until as much of the carbon is burned off as possible. Add 25 cc. of hot water and digest a few moments. Filter the solution into a 300 cc. flask. Wash the filter paper and unburned carbon well with hot water. Return to the dish and completely ignite. To the remaining ash add an amount of N/10 sulphuric acid equivalent to the amount of sodium carbonate used, digest for at least fifteen minutes either on the water bath or on a hot plate. Filter into the flask containing the first filtrate and titrate the excess of acid with N/10 sodium carbonate, using methyl orange as the indicator.

H. C. Reed,
Secretary.

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BUREAU OF EMPLOYMENT

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

The Secretary will be pleased to assist in bringing together chemists seeking employment and those in the trade desiring chemists.

Notice of positions wanted and positions vacant will be published in This JOURNAL and the *Weekly Letter* of the Tanners' Council.

COUNCIL MEETING HELD AT NEW YORK CITY JANUARY 20, 1922

Members present—F. H. Small, H. C. Reed, C. C. Smoot, III, G. W. Schultz, G. D. McLaughlin, R. H. Wisdom.

The resignation of J. S. Rogers as chairman of the committees for the Determination of the Sugar Content of Leather and the Determination of Sugar in Extracts was presented and it was voted that an effort be made to have Mr. Rogers retain the chairmanship and that pending his decision Mr. I. D. Clarke be appointed chairman, pro tem. to take charge of the two committees.

It was voted that a Bureau of Employment be established, to be handled from the office of the Secretary, and that a notice should be published in the JOURNAL and in the *Weekly Letter* of the Tanners' Council to the effect that the Secretary will be pleased to do what he can to assist in bringing together chemists seeking employment and those in the trade desiring chemists.

It was voted that the Secretary write a letter of appreciation to the Secretary of the Tanners' Council expressing in behalf of the Association appreciation of the assistance they are giving us in increasing the membership of the Association and the advertisements in the JOURNAL.

G. W. Schultz's proposals to change existing provisional methods with additions to official methods and to alter and add to the provisional methods for the analysis of sulphonated oils were duly approved by the Council. (See This JOURNAL, **16**, 525 (1921)).

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The Secretary was instructed to write to T. A. Faust requesting him to present the matter of the Determination of the Melting Point of Greases in a definite form for the consideration of the Council. (This JOURNAL, **11**, 92 (1916). See Committee Report).

A previous suggestion of R. W. Frey to reduce the amount of leather used for moisture determination was again presented to the Council by Mr. Frey and acted upon unfavorably by the Council. (See This JOURNAL, **16**, 228 (1921)).

A committee consisting of G. W. Schultz, Chairman, H. C. Reed and R. E. Porter was appointed to consider the advisability of increasing the amount of leather for nitrogen determination.

The matter of the specification for lime and the question of standardizing the material for use in the leather industry as presented by the American Society for Testing Materials and the National Lime Association was discussed. C. C. Smoot, III, chairman of a committee appointed by the Tanners' Council on such specifications reported progress.

The increase in the subscription fee from $2.50 to $3.50 for American Mutual members of the Society of Leather Trades' Chemists as proposed by the Secretary of that Society was duly approved by the Council and will be voted upon by the members at the next Annual Meeting of the Association. (See This JOURNAL, **16**, 524 (1921)).

A report of the financial standing of the Association by Certified Auditors was submitted and duly approved. This report will be found elsewhere in this issue.

A vote was taken by the Council authorizing the Secretary to pay Sigmund Saxe $500.00 to complete payment on the amount loaned the Association by Mr. Saxe in 1920.

The Council voted that JOURNAL volumes of the year preceding the current year should be sold at membership value.

Single numbers of volumes I to XV..... $0.75 each

Single numbers of volumes XVI and XVII..... 1.00 each

Single numbers needed to complete a volume for binding to be furnished at $.25 per copy less than the above prices.

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The location and date of the next Annual Convention was considered and the result of the deliberation of the Council will be found published elsewhere in this issue.

A Program Committee was appointed consisting of H. C. Reed, Chairman, G. D. McLaughlin and Dr. Allen Rogers.

The Council acting under the ruling of the by-laws presented the following list of nominees for office to be chosen at the coming annual meeting:

PRESIDENT

Blackadder, T.
Claflin, A. A.
Faust, T. A.
Mosbaugh, F. R.
Reilly, C. W.
Smoot, III, C. C.

VICE-PRESIDENT

Balderston, L.
Drueding, C.
Kerr, G. A.
Mosser, T. J.
Orthmann, A. C.
Rogers, J. S.

SECRETARY

Blair, C. A.
Evans, J. V. R.
Hurt, H. H.
Reed, H. C.
Phillips, R. O.
Veitch, F. P.

ORDINARY MEMBERS OF COUNCIL

Creese, G. T.
Downing, J. S.
Frey, R. W.
Griffith, R. W.
Mlejnek, V. J.
Oberfell, C. B.
Porter, R. E.
Sprague, F. O.
Seltzer, J. M.
Tolman, L. M.
White, E. W.
Whitmore, L. M.

H. C. REED, *Secretary.*

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AUDITOR'S REPORT YEAR ENDED DECEMBER 31, 1921

January 18, 1922.

The American Leather Chemists Association,
22 East Sixteenth Street,
New York

Dear Sirs:

We have audited the books and accounts of THE AMERICAN LEATHER CHEMISTS ASSOCIATION for the year ended December 31, 1921, and submit herewith a comparison of balance sheets at December 31, 1920 and 1921, as Exhibit I and a statement of income and expenses for the year ended December 31, 1921, as Exhibit II.

The operations of the Association for the year resulted in an increase of $1,185.10 in the surplus account as shown in detail in Exhibit II. This excess of income over expenses, together with the collections made on 1922 dues and subscriptions of $1,247.30, or a total of $2,432.40, resulted in increasing the assets $1,676.91 and reducing the liabilities by $755.49. Included in the latter amount was the payment of $500.00 on the loan from Mr. Sigmund Saxe.

The amount of cash on deposit at the Bank of the Manhattan Company was satisfactorily reconciled with a certificate furnished by them. A second Liberty Loan Bond, par value $1,000.00, has been deposited with the Citizens Savings Bank, Stamford, Conn., as collateral to a loan in the amount of $679.00. The amount of dues receivable ($442.50) is made up of $55.00 due for 1920 and $387.50 for 1921. All resignations have been charged off and we were informed that the above amount is collectible. The amount receivable for advertising ($522.06) results almost entirely from advertising in the December issue of the JOURNAL.

Insofar as we were able to ascertain, all liabilities at December 31, 1921, are reflected in the attached balance sheet.

We acknowledge with thanks the assistance given our representative by Miss Drisko.

Very truly yours,
ARTHUR ANDERSEN & Co.,
Accountants and Auditors.

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COMPARISON OF BALANCE SHEETS

December 31, 1920 and 1921

ASSETS	December 31 1920	December 31 1921	Increase or Decrease
Cash	$ 789.41	$2,295.52	$1,506.11
Second Liberty Loan Bond (Deposited as Security for Loan)	1,000.00	1,000.00	
Accounts Receivable—			
Dues	122.50	442.50	320.00
Advertising	471.36	522.06	50.70
Reprints, etc.	240.65	40.75	199.90
	834.51	1,005.31	170.80
Total Assets	$2,623.92	$4,300.83	$1,676.91

LIABILITIES AND NET WORTH

LIABILITIES:			
Loans Payable—			
A. L. C. A. (Secured by $1,000.00 Par Value Liberty Bond)	$ 679.00	$ 679.00	
Sig. Saxe	1,000.00	500.00	500.00
	$1,679.00	$1,179.00	$ 500.00
Accounts Payable	562.66	325.97	236.69
Austrian Relief Fund	18.80		18.80
Total Liabilities	$2,260.46	$1,504.97	$ 755.49
DEFERRED INCOME:			
Prepaid Dues and Subscriptions		$1,247.30	$1,247.30
SURPLUS	363.46	1,548.56	1,185.10
Total Liabilities and Net Worth	$2,623.92	$4,300.83	$1,676.91

The Association has as an asset under a separate account approximately $1100.00 to be used for reprinting back numbers of the JOURNAL.

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Statement of Income and Expenses for the Year Ended December 31, 1921

	Amount	
Income:		
Dues and Subscriptions	$5,160.60	
Sale of Journals and Reprints	645.58	
Advertising	4,900.72	
Sundry	4.70	$10,711.60
Expenses:		
Printing and Mailing Journal	$5,667.88	
Salary of Executive Secretary	2,080.00	
Editorial Expense—Ridgway, Pa.	619.91	
Council Meetings	15.00	
Annual Meeting—Atlantic City	450.20	
Insurance on Journals and Stock	92.38	
Interest on Loan	40.65	
Copyrighting	12.00	
Desk and Office Equipment	114.55	
Booklets—Directory of Officers and Members	73.55	
Purchase of Back Number Journals	18.80	
Collection and Bank Charges	9.80	
Stationery and Printing	233.10	
Supplies	37.85	
Multigraphing	30.55	
Miscellaneous Expenses	30.28	9,526.50
Net Income		$1,185.10

ANNUAL BUDGET FOR THE YEAR 1922

GENERAL ACCOUNT

Income Receivable:			
Dues		$4,600.00	
To General Expense:			
Secretary's Salary	$2,080.00		
Printing and Stationery, Etc.	200.00		
Postage, Express, Etc.	175.00		
Printing Membership Booklet	75.00		
Annual Meeting	700.00		
Council Meeting	25.00		
Typewriter	70.00		
Auditor's Report	125.00		
Interest on Loan	40.65		
Miscellaneous Expense	100.00		
		3,590.65	
			$1,009.35

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JOURNAL ACCOUNT

Income Receivable:			
Advertisements	$5,200.00		
Subscriptions	500.00		
JOURNALS, Volumes, Reprints	1,000.00		
		$6,700.00	
To JOURNAL Expense:			
Journal and Index	$5,000.00		
Reprints of Articles	575.00		
Binding Volumes	300.00		
Insurance and Copyright	104.00		
Editor's Compensation	275.00		
Abstracts and Translations	280.00		
Back Numbers and Miscellaneous	100.00		
		$6,634.00	$66.00
Total Increase Income Over Expense			$1,075.35

H. C. REED,
Secretary—Treasurer.

THE NINETEENTH ANNUAL MEETING
June 21st, 22nd, 23rd

Bigwin Inn, a summer resort located on Bigwin Island, in the Lake of Bays district, Highlands of Ontario, Canada, has been chosen provisionally by the Council as the place for holding the next Annual Meeting of the Association. Whether final arrangements are made to hold the meeting at Bigwin Inn will depend entirely upon the support given the idea by the membership.

The Inn is not scheduled to open until the 24th of June, but the management has agreed to open by the 21st so that our Association may have full and sole possession during the days of the Convention. The Inn offers an exceptional opportunity for combining business with pleasure and making out of our Annual Meeting an ideal summer vacation. It offers many features of entertainment, such as music, dancing, boating, bathing, lawn bowling, tennis and golf. An orchestra will play in the dining room during the luncheon and dinner hours and for two hours in the evening for dancing. The Anglo Canadian Concert Band, under the direction of Herbert L. Clark, the World's greatest cornet soloist, will give a special concert at some time during the Convention.

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The management of the Inn suggests that those members who may find it possible would do well to bring their wives and families, and the Council believes the suggestion an excellent one. A meeting place of the character of Bigwin Inn is something new in the annals of the Association and the President and Council are of the opinion that it might result in closer contact of the members of the Association and a better understanding through the companionship thus brought about.

The real difficulty that will suggest itself to the members is the remoteness of the Inn. In respect to this you will observe that the hotel rate quoted is lower than we have been obliged to pay at other conventions and this will to a considerable extent offset the greater railway fare in the case of some of our members and will more than offset it in the case of others.

The HOTEL RATE quoted is $6.00 per day, per person, American funds. The rate is the same whether one or two persons occupy a room, but the management prefers that if possible two persons occupy a room in view of the fact that the rooms are equipped with twin beds so that the usual inconvenience of being located two in a room is not experienced. Rooms generally are arranged in suites of two with bath room between or connecting, but suites of four rooms and two baths and suites of seven rooms and three baths are also available. This rate will apply until July 15th, after which time the regular rates will prevail. Special rates are offered for children, and members desiring information on this subject are asked to communicate direct with the Bigwin Inn management. The rate includes meals and every facility for entertainment that Bigwin affords, with the exception of boating and golf, which will be at a special rate for the Association.

The following are the RAILWAY FARES which were in effect during the season of 1921 to the Bigwin Inn and return. All fares mentioned include war tax:--(Excursion fares for the 1922 season have not been published as yet, but we have been informed by the railway officials that there is a possibility of the fares being somewhat reduced).

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Boston	$52.98
Chicago	44.96
Detroit	25.92
Buffalo	18.90
Cleveland	33.06
Cincinnati	44.30
St. Louis	60.05
New York	49.71
Washington	65.53

Sleeping car fares from the points mentioned are not shown, but in general we would say that from New York, Boston, and Chicago, a lower berth fare would be between $14.00 and $16.00 the round trip. Members will be asked to meet in Toronto at a certain time and a special train will take the members from Toronto to Huntsville, connecting there with a special steamer for Bigwin Inn.

If the Secretary receives the approval and promises of attendance of a sufficient number of members to warrant holding the meeting at Bigwin Inn, the necessary arrangements will be proceeded with, but if the above idea is not supported adequately, another location will be decided upon.

THE PROPERTIES AND ACTION OF ENZYMES IN RELATION TO LEATHER MANUFACTURE *

By Joseph Turney Wood

The Soaking Process

Enzymes occur in and influence almost all the operations of tanning from the moment that the skin is flayed until it is dried out in the form of leather. The fresh skin contains a number of emzymes about which very little is known and other enzymes are soon formed by bacteria. We shall not consider these in any detail, as we may assume that the raw skin has been properly preserved after flaying and before coming into the hands of the tanner, but in the soaking process we meet with enzymes secreted by a variety of species of bacteria. Most of these bacteria liquefy gelatin by means of the proteolytic enzymes which they secrete,

* Reprinted from *J. Ind. and Eng. Chem.*, 13, 1135 (1921).

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and consequently they attack the skin. So far as the writer knows, the bacteria of the soaks have not been specially studied except by Andreasch,[1] who isolated a number of species of bacteria from the soaks. He identified the following:

B. fluorescens liquefaciens (Flügge)
B. megaterium (de Bary)
B. subtilis
B. mesentericus vulgatus
B. mesentericus fuscus
B. mycoides (Flügge)
B. liquidus (Frankland)
B. gasoformans (Eisenberg)
White bacillus (Maschek)
Proteus vulgaris
Proteus mirabilis
B. butyricus (Huppe)
White streptococcus (Maschek)
Worm shaped streptococcus (Maschek)
Gray coccus (Maschek)

All these may be classed as putrefactive organisms, and they secrete a variety of enzymes, some of which act energetically on the hide substance. In view of the fact that the enzymes in the the soaks are nearly all derived from bacteria, it is evident that the soaking should be carried out under antiseptic conditions as far as possible.

Rideal and Orchard[2] examined the action of *B. fluorescens liquefaciens* on gelatin to which was added ten per cent Pasteur's solution to serve as nutrient medium. The gelatin was completely liquefied in 3.5 days. It was shown that the liquefaction of gelatin was due to an enzyme, or enzymes, secreted by the bacteria. The liquefied gelatin was alkaline and had a slight putrefactive odor, but contained no hydrogen sulfide. A notable feature was the small amount of ammonia and volatile bases produced; only 0.2 g. of ammonia per 100 cc. were produced even after 16 days' incubation. The liquefaction of gelatin by pancreatic trypsin takes place with much greater rapidity; 0.2 mg. of the enzyme preparation will liquefy 5 cc. of 4 per cent gelatin in 30 min. at 39°.

[1] *Gerber*, 1895-6.
[2] *Analyst*, October, 1897.

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The Lime Liquors

In a lime liquor through which skins have passed, there are enzymes present. The writer is inclined to believe that some of these are from the skin itself, at least when fresh market skins are worked, as for example, the tissue enzymes, but nothing definite is known of these. Bacteria, however, develop in the limes. *B. prodigiosus* and *Micrococcus flavus liquefaciens,* both of which are known to produce proteolytic enzymes, have been identified. These enzymes decompose the dissolved skin substance into gelatones (gelatin-peptones) and eventually into amino acids, caproic acid and ammonia. It is very probable that the enzymes in the limes act in the same way as the enzymes in the sweating process of unhairing, but in the limes the process stops short of putrefaction, whereas in the sweating stove it may go on until the skin is run on the grain.

The Bating Process

The investigation of the action of the bates or puers has proved of great interest and has resulted in the use of scientific methods depending on the use of commercial enzymes in leather manufacture. The object of bating or puering is to render the skins, and the resulting leather, soft and supple. Skins which have undergone the liming process must be thoroughly freed from lime before going into the tan liquors, and for light and soft leather they must be reduced or "brought down" so that the elasticity or resilience of the skin fibers is got rid of, and the skin when tanned can be stretched without springing back. In the case of the old manure bates for light leathers, this is done by passing the skin through a bate or puer composed of an infusion of dogs' dung in water at a temperature of 35° to 40° until the desired result is obtained. This condition is known to the workman by the feel of the skin. The process has been in use from the very earliest times, but until comparatively recently no explanation of the action of the dung bates was satisfactory.

Thirty years ago, when the author commenced the investigation of the action of the dung bate in the manufacture of light leathers, he came to the conclusion that a great part of the bating effect was due to the action of proteolytic enzymes on the skin in conjunction with ammonium salts present in the bate. The latter not only

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combined with the lime remaining in the skin, but also acted as activators for the enzymes. Numerous experiments were made on skins both in the presence of growing bacteria and of the products of the bacteria, precipitated by alcohol, and it was found that when suitable ammonium salts were present the bating action in both cases was similar.

There is little doubt that every variety of enzyme, hydrolyzing, oxidizing, ammoniacal, etc., is produced by bacteria. The production of enzymes by bacteria was observed by Wortmann in 1882, and Fermi and others have investigated the enzymes of the bacteria which liquefy gelatin. Since the bacteria in the bate produced these enzymes, the first idea was to use them in practice in a scientific way. In conjunction with Prof. H. Becker, we manufactured a bacterial bate "Erodin," which the writer believes was the first attempt to apply the use of pure cultures of bacteria in the leather industry. The bacterium used was a variety of *B. coli* isolated from dog dung. Harden[3] has shown that this bacterium produces at least three enzymes.

An investigation of the enzymes contained in dog dung showed that five different enzymes were present[4]:

1—A peptic enzyme resembling stomach pepsin.
2—A tryptic enzyme, or enzymes, resembling pancreatic trypsin.
3—A rennin (coagulating enzyme).
4—An amylolytic enzyme.
5—A lipase.

In view of the fact that the bate solution is alkaline, it seemed pretty certain that trypsin must be the principal enzyme acting, and it is this enzyme which has been applied practically in the manufacture of artificial bates.

It must be clearly understood that, although the enzymes and ammonium compounds are the chief bodies acting on the skin in the dung bate, they are not the only bodies taking part in the process. As the writer has shown, there are many other bodies in the dung which act in a way at present not understood. Among these the fats, soaps, and phosphates are, in his opinion, important. Among other enzymes present in the dung, the lipases have a considerable effect in emulsifying and hydrolyzing the fats.

[3] *Chem. World*, 1912, 403.
[4] *J. Soc. Chem. Ind.*, 31 (1912), 1105.

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Skins which have been overlimed are bated more effectively in a dung bate than in an artificial, enzyme bate, and this must be due to some constituents in the dung bate which are absent from the enzyme bate. It has further been shown that excessive liming so alters the chemical constitution of the hyaline membrane as to render it capable of being attacked by trypsin.

Rosenthal[5] states that elastin is digested in the bating process; and more recently Seymour-Jones has been able to show that the elastin is contained principally in the grain layer.

Elastin is the characteristic constituent of the elastin fibers which remain after treating the skin with boiling water, caustic alkali, dilute hydrochloric acid, alcohol, and ether. It is of pale yellow color and is insoluble in any menstruum which does not act on it chemically. When boiled with strong hydrochloric acid and stannous chloride, leucine (30 to 40 per cent) and a small quantity of tyrosin (0.25 per cent) are found among the products of its decomposition, together with ammonia, glycine, and amino-valerianic acid, but not aspartic or glutamic acid. This behavior distinguishes elastin from both proteids and gelatin, since the former yield aspartic and glutamic acids but no glycine, while gelatin never yields a trace of tyrosin. Elastin is digested by the body enzymes. It is allied to the fibroin of silk and spider web.

Quite independently J. A. Wilson[6] has shown definitely that the elastin of the skin is removed by the tryptic enzymes of the bate. In the unbated skin the elastin fibers are fairly dense in the grain layer. As the bating proceeds, they gradually disappear, and at the end of 24 hours the grain is quite free from elastin. In skin delimed with ammonium chloride only, the elastin was left apparently unaltered. Wilson concludes that the mechanism of bating consists of two distinct parts: (1) reducing the limed skin to a condition of minimum swelling, and (2) digesting the elastin fibers present in the outer layers of the skin. It may be added that Mr. Seymour-Jones considers the so-called hyaline layer to be really the deepest layer of the epithelium, and proposes to call it the grain membrane, as being more in harmony with the nomenclature of the leather industry. In light leather manu-

[5] "Biochemical Studies of Skin," *J. A. L. C. A.*, 11 (1916), 463.
[6] *J. Ind. and Eng. Chem.*, 12 (1920), 1087. THIS JOUR., 15, 649 (1920).

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facture it is what is called a "flywing" and yields practically no gelatin on boiling, whereas the split flesh is wholly transformed into gelatin.

Although the elastin is completely removed from the skins bated by trypsin for a sufficiently long time, about 24 hours, in practice the bating is not continued to this point, but is carried on for only about 2 to 6 hours. The elastin is only partly removed in this time, but the skins made good leather. The writer believes that it is not necessary, or even desirable, for the whole of the elastin to be removed or dissolved in order to let the skin down, but that it is sufficient for the elastic fibers to be broken up or weakened, in order that the desired suppleness may be obtained.

There still remain many unsolved problems in the bating process; these are being pursued with vigor, and the writer looks forward confidently to the time when we shall be able to bate any kind of skin by means of artificial bates suitable to the particular leather required.

Drenching

In the manufacture of many kinds of light leathers, skins are drenched after bating. This process usually consists in placing the skins in a mixture of bran and water (5 to 10 g. per liter) at a temperature of 30° to 35°. This ferments vigorously for 18 to 24 hours, with evolution of a considerable quantity of gas and the formation of weak organic acids. In a drench taken in actual work, the gases had the following composition:

	Per cent
Carbon dioxide	25.2
Hydrogen sulfide	Trace
Oxygen	2.5
Hydrogen	46.7
Nitrogen	26.0

The acids produced per liter were:

	Gram
Formic	0.0306
Acetic	0.2042
Butyric	0.0134
Lactic	0.7907

Of other bodies formed during drenching, the quantity is insignificant, trimethylamine being the chief. It has been shown that the starch of the bran is converted into glucoses and dextrin

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by the action of an amylolytic enzyme, cerealin, allied to diastase. This enzyme was discovered by Mege Mouries[7]. It resembles the diastase of translocation described by Brown and Morris[8] in their work on the germination of grass seeds. It transforms starch into dextrin and glucose, whereas ordinary malt diastase transforms starch into dextrin and maltose. The action of cerealin is much slower than that of diastase. Dr. W. H. Wilcox and the author found that in 12 hours at 40° about one-half the starch is transformed. With malt extract, the whole of the starch disappears in about 2 hours. The glucoses are then fermented by bacteria (*Bacillus furfuris*) with the formation of the organic acids above mentioned. The principal acid produced is lactic; the acetic acid is produced directly from the glucoses without any preliminary alcoholic fermentation by yeasts.

The mode of action of the drench on the skins is as follows:

1—Solution of the last traces of lime not removed by the bate and the subsequent swelling action of the organic acids on the skin fibers. The acids also dissolve a small amount of skin substance.

2—Distension and floating of the skins by the gases produced by the fermentation.

3—Mechanical absorption of dirt by the particles of bran or flour in the drench.

It will thus be seen that the action of enzymes in the drench is an indirect one.

Tan Liquors

In the tan liquors changes go on which are brought about by enzymes; some of these are secreted by molds and yeasts and others are present in the plants from which the tanning materials are extracted. Unfortunately very little is known about these enzymes, but attention should be called to the work of Fernbach[9] in France, who prepared an enzyme which he called tannase from the mold *Aspergillus niger*, obtained from gall nuts. He cultivated the mold in Raulin's liquid, using tannin in place of the sugar. The product was macerated in water, the maceration concentrated at a low temperature *in vacuo*, the liquid precipitated by alcohol, and the precipitate treated exactly as in Lintner's method for the preparation of amylase. The gray powder thus

[7] *Compt. rend.*, 37 (1853), 351; 38 (1854), 505; 43 (1856), 1122; 48 (1859), 431; 50 (1860), 467
[8] *J. Chem. Soc.*, 57 (1890), 458.
[9] *Compt. rend.*, 26 (1848), 1214; *J. S C. I.*, 20, 137 (1901).

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obtained, when dissolved in water, acted rapidly on tannin at 50°, converting it into gallic acid. The solution of tannase filtered through a Chamberland filter into a sterilized solution of tannin acted just as effectively, proving that the action was due to an enzyme and not to a fermentation through the agency of organized cells.

H. Poltevin[10] prepared a solution of tannase by a process similar to that of Fernbach, but independently of him. Along with the gallic acid formed there is also a variable amount of glucose in the case of commerical tannins, but he considers these commercial tannins as mixtures. From a purified tannin he obtained gallic acid corresponding to 98.5 per cent of the tannin. The fact that tannase also hydrolyzes phenyl and methyl salicylates lends support to Schiff's formula for tannin, $C_6H_2(OH)_3.COO.C_6H_3(OH)_2.COOH$. In nature tannin is often accompained by gallic acid. No doubt the latter is formed by the action of tannase, which Poltevin found to exist in sumac leaves, and which no doubt occurs in other substances containing tannin.

ESTIMATION OF REDUCING SUGARS IN TANNIN EXTRACTS OF ANALYTICAL STRENGTH

By H. Leslie Longbottom

Received January 14, 1922

An important matter in the examination of new materials for tanning purposes is the estimation of the reducing sugars in the liquid extracts. In routine analysis of such materials it is a considerable saving of time if the analytical solutions prepared for the official hide powder method of tannin estimations can be used without concentration for the estimation of sugars. Such solutions contain as a mean value about 0.03 per cent sugars: the term sugars being applied to compounds which reduce Fehling's solution and which are left in solution after removal of tannins and colouring matters.

The following methods for removing colouring matters, tannins, etc., and for the subsequent estimation of the sugars in such solutions have proved successful in this laboratory.

[10] *Compt. rend.*, 26 (1848). 1215; *J. S. C. I.*, 20, 137 (1901).

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1. To remove tannins, colouring matters, etc., from vegetable extracts a solution of either the basic or neutral acetate of lead is usually employed. It has been shown by Veitch and Rogers that the basic acetate if used in excess will remove with the precipitated tannins appreciable quantities of sugar from solution. The neutral acetate on the other hand does not wholly precipitate tannins, colouring matters and other substances not sugars, which may reduce Fehling's solution and so be estimated as sugars. This is evidenced by a colouration of the filtrate, after precipitation with normal acetate of lead, by iron salts and by a subsequent precipitation with basic acetate of lead. Thus each solution has its advantage and its disadvantage and by a suitable use of both reagents it was hoped to utilise each advantage and to eliminate the disadvantages.

To 200 cc. of the solution of analytical strength add 10 cc. of a saturated solution of neutral lead acetate and allow to stand 20 minutes, stirring occasionally. The solution may be left to stand overnight if sufficiently well preserved. Filter; collect 160 cc. of filtrate which will give an acid reaction to litmus; make *just* turbid by the addition of 5 N sodium hydroxide solution. This point must be carefully watched by stirring well and waiting a few seconds after addition of each drop of caustic solution. Usually three to five drops are sufficient. Add 5 cc. basic acetate of lead solution.[1] Allow precipitate to settle during twenty minutes; filter and collect 150 cc. Add 15 cc. of a saturated solution of sodium sulphate (approximately 19 per cent sodium sulphate); stir well and allow to stand till supernatent liquid is clear. Since a volumetric method is used for sugar estimation there is no need to remove lead remaining in solution as sulphate after the above treatment—it does not affect the subsequent titration. When the precipitate has settled, filter and wash with a minimum of water. In order to invert add to the filtrate 5 cc. concentrated hydrochloric acid and heat the flask in boiling water for 1½ hours. Cool, neutralise with 5 N sodium hydroxide solution and make up to 200 cc. Filter and take 50 cc. for titration as below. All solutions so obtained have been either very faintly coloured or quite colourless.

[1] Leather Chemists' Pocket Book, Procter, p. 171.

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The following table gives a comparison of the three methods of removing tannins and colouring matters and is a fair indication of many similar results.

TABLE I.

Solution	Clarifying reagent	Appearance after inversion	Sugar in solution
			%
A.			
	Neutral acetate of lead	Very highly coloured	.066
	Basic acetate of lead	Very faintly coloured	.003
	Both solutions as outlined	Faintly coloured	.008
B.			
	Neutral acetate of lead	Very highly coloured	.063
	Basic acetate of lead	Very faintly coloured	.003
	Both solutions as outlined	Faintly coloured	.006

The methods were applied to a new tannin extract (Marri Kino) known to contain a compound that is not precipitated with neutral acetate but is precipitated with basic acetate and will reduce Fehling's solution even in the cold. Thus this substance, evidently not a sugar, is estimated as such if neutral acetate alone is used as clarifying agent. There is a tendency for the removal of sugars with the precipitation by means of basic acetate of lead. The two solutions used in the manner suggested remove tannins and colouring matter almost as well as basic acetate alone.

2. These solutions will rarely, if ever, contain more than 0.1 per cent reducing sugars calculated as glucose and the following scheme of titration has been found to give good results. This method was suggested by Mr. R. A. Fowler, B. Sc., A. I. C. Officer in charge of this laboratory, who found it quite satisfactory for the estimation of sugars in wood.

Prepare a standard solution of glucose 0.5 per cent according to the method of the American Leather Chemists' Association. Dissolve 4.75 grams of pure cane sugar in 75 cc. of water. Add 5 cc. concentrated hydrochloric acid and heat at 70° C. for seven minutes. Cool rapidly and exactly neutralise with N sodium hydroxide. Make the solution to 1,000 cc. The solution will keep well if preserved with a few drops of toluene.

This solution is used to standardise Fehling's solution prepared by dissolving 34.64 grams of copper sulphate with 10 cc.

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of normal sulphuric acid in 500 cc. of water; and a second solution of 70 grams sodium hydroxide with 175 grams of Rochelle salt in 500 cc. of water.

Dilute 10 cc. of mixed Fehling's solution with 50 cc. of water and titrate in the usual way using the outside indicator described by Harrison in the *Pharmaceutical Journal*, 1903, p. 170. This consists of a solution of potassium iodide (1 in 8) to which a few drops of a 1 per cent starch solution has been added. It is essential that this solution be absolutely fresh. Take one drop of the potassium iodide-starch solution and acidify with one drop of a ten per cent acetic acid solution on a spot tile. Remove from the titration solution a drop on the end of a glass rod and just touch the surface of the liquid on the spot tile. A blue colouration indicates unreduced copper in solution. The end point by this means may be determined to 0.1 cc. of a 0.5 per cent standard sugar solution. The indicator may require a little experience but with use concordant results are obtained.

For the estimation of sugars in the weak clarified solutions dilute ten cc. of mixed Fehling's solution with 50 cc. of the clarified sugar solution and titrate excess Fehling's with the standard sugar solution as before.

If the above quantities be used and if—

s be the number of cc. of standard solution equivalent to 10 cc. Fehling's solution

and *n* be the number of cc. standard solution required to complete the reduction of 10 cc. Fehling's solution diluted with 50 cc. of the clarified sugar solution;

then,

$(s-n)$ 0.0145 gives percentage of reducing sugars calculated as glucose in the original solution.

In testing the above method duplicate analyses were conducted, to one of which a known quantity of sugar was added and this quantity was then estimated as the difference between the two results. The sugar was added either in the form of a solution of invert sugar or of a solution of sucrose calculated to invert sugar; as indicated in the table.

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The following table gives the results obtained.

TABLE II.

Solution Ref. No.		Sugar added %	Sugar in solution %	Difference %	Discrepancy %	
I 16	iv	0.025 (glucose)	0.0367	0.023	—0.002	
		—	0.0136	—		8%
I 16	ii	0.024 (glucose)	0.0377	0.0232	—0.001	
		—	0.0145			4%
I 16	iv	0.024 (glucose)	0.0436	0.023	—0.001	
		—	0.0203			4%
I 16	v	0.024 (glucose)	0.032	0.022	—0.002	
		—	0.010			8%
I 17	no 6	0.012 (glucose)	0.018	0.012	——	
		—	0.006			
P 41		0.0386 (sucrose)	0.1062	0.0359	—0.0027	
		—	0.0703			7%
P 42		0.0219 (sucrose)	0.0262	.0207	—0.0012	
		—	0.0055			5%
T 5		0.025 (glucose)	0.055	0.026	+0.001	
		—	0.029			4%
T 3		.025 (glucose)	0.077	0.021	—0.004	
		—	0.056			16%
T 8		0.012 (glucose)	0.029	0.013	+0.001	
		—	0.016			8%
T 11		0.012 (glucose)	0.054	0.011	—0.001	
		—	0.043			8%
T 15		0.040 (sucrose)	0.0855	0.0372	—0.0028	
		—	0.0483			7%
T 19		0.012 (sucrose)	0.029	0.012	——	
		—	0.017			
T 21		0.012 (sucrose)	0.039	0.012	——	
		—	0.027			
T 22		0.1542 (sucrose)	0.1556	0.1542	——	
		—	.0014			
T 28		0.0425 (sucrose)	0.0760	0.0456	+0.0031	
		—	0.0304			7%

SUMMARY

1. The use of normal lead acetate for the precipitation of tannins and colouring matters is not found satisfactory with some tannin liquors.

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2. Basic lead acetate alone is apt to carry down sugars with the precipitate.

3. By the use of the method suggested above the bulk of the tannins, etc., is removed by normal lead acetate in slightly acid solution and the subsequent precipitation with basic lead acetate is of small bulk and removes the remaining tannins and colouring matters with little chance of the adsorption of sugars.

4. The scheme of titration with outside indicator gives a reasonably accurate estimate of reducing sugars in very dilute solution.

5. The method is useful for the estimation of reducing sugars in dilute vegetable extracts without concentration.

FOREST PRODUCTS LABORATORY,
Perth, Western Australia, December, 1921.

SOME THOUGHTS ON THE MEASUREMENT OF THE PLUMPING VALUE OF TAN LIQUORS

By H. C. Reed and T. Blackadder

Received January 20, 1922

No little interest has been aroused of late over the possibility of determining the plumping power of a tan liquor with the aid of hide powder.[1] The methods of Porter and of Wilson depend upon noting the bulk of swelled powder and that of Claflin on the water drained away from swelled powder.

Of the methods suggested that of Claflin seems to offer the best opportunities of development into a working method as the two former methods would seem to be more apt to influence by the texture and size of the hide powder particles, and further the principle involved appears more capable of adaptability to accuracy and ease of manipulation. There are, however, several points not hitherto touched upon that would appear worthy of due consideration, and some of these may be of fundamental importance in shaping a feasible method.

In the first place let us consider the question of the hide powder itself. Air dry hide powder contains a variable quantity of water. It is true that the variation is small but would nevertheless be of some consequence particularly if we desired to

[1] *J. A. L. C. A.*, 1921, p. 562, 571. *J. S. L. T. C.*, 1921, p. 259.

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establish a standard water-retention figure, doing away with the necessity of running a blank determination with every individual set of plumping tests conducted. The advantage of such a standard is obvious. A solution of the difficulty might be in the use of a hide powder previously wet out and squeezed to a predetermined water content. Such a powder would offer the advantage of a greater weight giving greater accuracy when weighing out. This point is worthy of consideration when we remember that quantities as small as two grams are sufficient for this method.

Again, the hide powder we use has a certain acid content. It would appear preferable to use a neutral hide powder. With an acid hide powder the swelling effect of the acid liquor must be additive to the swelling effect of the acid present in the hide powder itself. The rate and degree of swelling due to the acid liquor should decrease with the increase in the degree of acidity of the hide powder, and the relative difference in maximum swelling of acid hide powder with acid liquor to acid hide powder with water must be less than that of neutral hide powder with acid liquor to neutral hide powder with water.

Further, our standard hide powder contains lime, and the lime will form salts with the acids of the liquors. It has been amply proven that salts have a repressing effect upon the swelling of hide and would therefore vitiate our experimental work by superimposing their repressing effect on the acid swelling effect. This might be of little moment were it not for the fact that no corresponding repressing effect will occur in the water blank owing to the absence of these salts. A neutralized hide powder free from lime and salts can be made from our present acid hide powder by deliming with formic acid, washing, neutralizing with soda and rewashing.[2]

It may be of interest to note the results given by acid and neutral hide powders with N/100 solutions of lactic and butyric acids.

	Lactic	Butyric
Cc. drained off from acid hide powder	56	76
Cc. drained off from neutral hide powder	71	84

[2] Also see C. R. Smith, *J. A. C. S.*, 43, 1350 (1921). Description of method for preparing ash free gelatin.

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These tests were run using an amount of hide powder representing two grams of absolutely dry hide powder to 100 cc. N/100 acid, allowing for the water in the hide to make up the 100 cc. The neutral hide powder was neutralized with 33 cc. N/10 alkali to 25 grams air dry hide powder, washed four times, squeezed to 75 per cent water, 8 grams of wet hide powder being used. The fourth wash gave no test for chlorides or lime.

Reference to the report of the committee on the measurement of plumping by the Claflin method (This JOURNAL 1921, page 562) shows that considerable difficulty is experienced in the mechanism of the method. Trouble is had in properly transferring hide powder and liquor to funnel and from absorption of liquor in filtering by paper, cotton-plug or cloth. All these difficulties are in one direction of reducing the volume of acid liquor. It would appear to the writers to equally merit criticism that so many distinct pieces of apparatus should be required for a test seemingly so simple. The suggestion is made that the apparatus described below, and which has proved adapted for the purpose in the writers' laboratory, be given a trial.

The method obviates loss of liquor in transferring from one vessel to another, and since the liquor retained by the cotton plug after draining into the measuring cylinder is equivalent to the water held by the cotton plug when originally wet out no correction for absorption is necessary. The dilution of the acid liquor by the water in the cotton plug may be neglected. The manipulation is simple and little attention required.

It is hoped that the suggestion may be of aid to the committee having in charge the application of the Claflin method to tannery liquors, and to others desiring to try out a method for the measurement of plumping value. The plumping value of various acids is readily ascertained by the procedure given.

It would appear as though the Claflin method should give significant results on weak tannery liquors; those with relatively low tannin content. Just what idea might be gotten of the plumping value of liquors relatively strong in tannin is somewhat more problematical. It is conceivable that such liquors may give a negative plumping value if the astringency of the tannin has greater contracting effect than the acid has swelling

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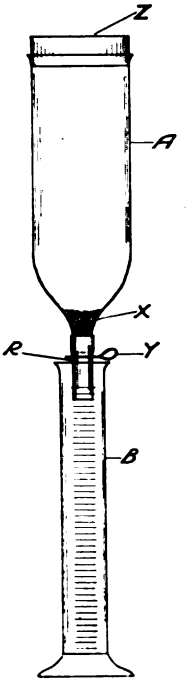

Description:—

A—Percolator, with rubber tube connection R and pinchcock Y.
Z—Rubber stopper, X—cotton plug inserted in neck of A.
B—Graduated cylinder.

Operation:—

Cotton plug X is saturated with water, pinchcock Y being open and allowed to drain. Pinchcock Y is closed and the hide powder introduced into A. A definite volume of acid liquor is added, stopper Z inserted and A agitated if necessary to assure through mixing of hide powder and liquor. The agitation may be repeated several times and sufficient time allowed for swelling by permitting to stand over night. In the morning pinchcock Y is opened and liquor allowed to drain into graduated cylinder B.

effect. Such a contingency does not imply that the liquor is without plumping value, since in the absence of acid the contraction of the hide powder would be greater and the volume of liquor drained off greater. Thus it is possible that the method might have to be interpreted from its measure of negative as well as positive plumping value.

It must be remembered that the Claflin method is based on the swelling effect of acid on raw hide powder while the acids of tannery liquors are for the most part functioning on leather

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of varying degrees of tannage. The plumping value of acids in tannery liquors might possibly best be ascertained after removal of tannin; say for example, after precipitation of the tannin with gelatin. With liquors of relatively high tannin content the function of the acids is in assisting penetration of tannin and fixation of coloring matters and the phlobaphenes—that are so closely related to the tannins. Non-acid liquors will not tan. Tannin expels acid during the tanning process and crowds it toward the tail, its ultimate usefulness being found in the neutralization of lime and in the swelling, or retention of swelling, of hide in liquors of relatively low tannin content.

Too great negative swelling in stronger liquors would convey a warning. If in such liquors acid is not present in proper amount it will fall short of proper amount in weaker liquors. The question resolves itself into the standard of plumping value, and as to whether there can be a general standard or whether standardization must be for each individual tan yard and be relative.

The importance of the measurement of the plumping effect of acid solutions, either alone or in conjunction with tan liquors or with salt solutions, is important from the theoretical as well as from the practical viewpoint. From both points of view it has been recognized that a mere titration of the acids present in a tan liquor leaves much to be desired as to the information obtained. Practical experience has proved that all acids are not alike in respect to their power to plump and some other measure than a titration is needed. From the practical aspect it would appear that the empirical method suggested by Claflin should be capable of being developed to give the information required. In the developing of the method and in the interpretation of the results obtained a few theoretical considerations would appear worthy of our attention.

A great amount of attention has lately been focussed on the hydrogen ion content of tan liquors, largely owing to the work of Procter and Wilson[3] on the swelling of gelatin in solutions of hydrochloric acid. Less attention has been attracted by Bennett's[4] articles on the lyotrope series. Unfortunately there

[3] Procter and Wilson, *J. A. L. C. A.*, XI, 261 (1916).
[4] H. G. Bennett, *J. A. L. C. A.* XIII, 91, 270 (1918).

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has seemingly been too much inclination for various workers to ride their own hobby horse with the result that the general advance of our combined knowledge has been delayed.

When we consider the immense amount of work which has been done on the swelling of proteins by acid solutions we cannot accept any single theory yet put forward as final. We have experimental[3] [5] [6] data enough to indicate that gelatin and hide powder are very similar in showing increasing swelling with either increasing acid or increasing alkali content up to a maximum. This maximum is followed by a decline, more pronounced on the acid than on the alkaline side in the case of hide powder[7] and very much alike in the case of ash free gelatin.[6] But we are not in a position to say that all acids would produce the same swelling when present in concentrations sufficient to produce the same hydrogen ion concentration. In fact we would from the present extent of our knowledge expect that they would not. While it has not been explicitly claimed that the concentration of the hydrogen ions is the sole determining factor in the swelling of gelatin and, by parallel, hide, there have been such strong claims made for recognition of its importance that many appear to have taken it for granted that it is the sole determining factor or at least by far the most important factor. Is not any method based on electrical measurement of the plumping power of solutions by the potentiometer tacitly assuming this?

It would appear without going very far below the surface in our theoretical discussion that the influence of salts upon the swelling of gelatin and hide is worthy of more attention than the leather chemist is giving it to-day. We know almost as an axiom that salts repress swelling but have we noted how different salts differ in effect? McLaughlin[8] [9] in his experiments on fresh steer hide includes figures which while not specifically directed at this phase of the question surely attract attention to it. His figures show very different values of swelling obtained by each of several acids when different salts are present. Bennett[10] has

[5] C. R. Smith, *J. A. C. S.*, 43, 1350 (1921).

[6] E. C. Porter, *J. S. L. T. C.*, 5, 259 (1921).

[7] Unfortunately Porter does not specify that ash free hide powder was used which, in conjunction with the salts used in solution might influence this result.

[8] G. D. McLaughlin, XVI 295 (1921).

[9] McLaughlin and Porter, *J. A. L. C. A.*, XV, 557 (1920).

[10] H. G. Bennett, *loc. cit.*

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directed attention to the Hofmeister series but has failed to draw conclusive parallels. In fact with such a paucity of data on the influence of salts on the swelling of gelatin it would be out of the question to draw any convincing parallels. But an examination of the figures in McLaughlin's work would seem to yield evidence of a possible parallelism between the relative effects of the salts examined and the order of their radicals (metal and acid) in the Hofmeister Series.

That the influence of salts needs more extensive study may be seen from one or two further considerations. For instance Thomas and Baldwin[11] have given us figures to show that the addition of common salt to solutions of hydrochloric acid cause an increase in the hydrogen ion concentration of these acid solutions to a very considerable extent and despite this increase in hydrogen ion concentration we have the practical experience of salt reducing the swelling of gelatin or hide. Here it would appear that the influence of the salt acting as a depressant outweighs the influence of the hydrogen ion acting as a swelling agent, and yet we suffer from a lack of knowledge of the quantitative effect of this salt action.

Further we have every reason to expect that salts will vary in their repressing value and that this variation will depend in part upon the metallic radical (kation) and in part upon the acid radical (anion) present in the salt. If this expectation proves to be correct then we are led to an inevitable conclusion, namely that since anions possess a varying repressing effect when present in a salt they possess it also when present in an acid. Which means that various acids have different swelling powers independent of their strength (or ability to yield hydrogen ions in solution). This information must be sought in salt solutions as the effect of the incomplete ionization of weaker acids and the effect of the hydrogen ion complicate the study in acid solution to a hopeless degree.

Until we have a greater fund of knowledge on the question of the effect of salts in solution upon the swelling of gelatin or hide substance it is only bewildering to theorize extensively, however great the temptation.

CONTRIBUTION NO. 6 FROM THE REED LABORATORIES.

[11] *J. A. C. S.*, 1919.

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THE CHEMICAL CONSTITUENTS OF SKIN*

By F. L. Seymour-Jones

It is the object of this paper to present very briefly a survey of the chemical constituents of skin, regarded, as far as may be possible, as chemical individuals. In recent years two general papers on skin chemistry have appeared, one, written about 1910 but published posthumously, by R. A. Seymour-Jones,[1] ** and the other, published in 1920, by G. L. Terrasse.[2] These summarize the work on the subject, but deal more particularly with the structure of the hide proteins and the conception of amino acids as "Bausteine" in protein composition. It is proposed in the present paper to deal with matters unconsidered in the above papers, or from viewpoints which have arisen since their compilation.

Work on the Swelling of Gelatin

The work of Procter[3] and his collaborators on the acid swelling of gelatin has proved of fundamental importance in dealing with proteins in general. This has resulted in the deduction of mathematical formulas by which the distribution of ions in the gelatin (or other protein) and in the external solution can, under given conditions, be calculated. In place of a series of obscure phenomena, necessitating individual measurements for each case, we now have a definite stoichiometrical relationship based on applications of osmotic equilibria and Donnan's theory of membrane equilibria.

This theory of gelatin swelling depends, however, on a definite conception of the molecular structure of gelatin. Procter regards gelatin jellies and solutions as composed of a network of molecular dimensions. This permits the development of osmotic effects, while ions within the jelly remain within the range of molecular attractions. In a protein jelly the term "molecular" may, however, cover a relatively large space. Bütschli has formulated a theory in which the jelly is presumed to have a network of microscopic dimensions, while Quincke considers a jelly to be of two phases, a colloid-poor and a colloid-rich phase, the

* Reprinted from *J. Ind. and Eng. Chem.*, 14, 130 (1922).

** Numbers in the text refer to Bibliography.

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one dispersed in droplets throughout the other. This last view has met with considerable support, but, on the whole, the evidence favors Procter's view.

Work on Isoelectric Point of Proteins

Arising from the work on gelatin swelling, most important results have been obtained in the researches of Jacques Loeb,[4] who has clearly shown the importance of taking into account the isoelectric point of proteins and the hydrion concentration of solutions employed. The isoelectric point (I. E. P.) has been shown to be, for proteins in general, coincident with the points of minimum swelling, conductivity, osmotic pressure, viscosity, and solubility. For gelatin,† determinations vary from pH 4.5-4.7, and the value may be taken as about 4.6. No figures have been published yet for skin proteins in general, but work at Leeds University on hide powder gives the figure 4.8 for collagen.

The importance of this figure lies in the fact that proteins in general are amphoteric. Loeb has shown for gelatin, and the same probably applies to hide proteins in general, that at a pH greater than its isoelectric point it functions only as an acid, and at a less pH only as a base. Thus, when gelatin was treated with silver nitrate and subsequently washed to remove excess of the salt at pH 3.6 to 4.7, no silver combined with the gelatin, whereas above 4.7 silver combined with the gelatin. Below 4.7 gelatin nitrate exists and above 4.7 silver gelatinate.

As a practical example, consider the disinfection of raw hides with formic acid and mercuric chloride. Under the conditions specified by the process, the pH is such that no mercury can combine with the hide substance. Consequently if the hides are washed prior to liming (or other alkaline treatment) all the mercury is removed. If the mercury ion is not so removed, it will be fixed in the limes, and black stains will occur in subsequent processes.

Using equivalent solutions of bases, Loeb found that all monacid bases gave a swelling, viscosity, and osmotic pressure practically identical, but considerably greater than di-acid bases. The same applies to acids; all functioning as monobasic acids gave practically identical curves, while dibasic acids (*e. g.*, sulfuric,

† Michaelis, 4.7; D. Jordon Lloyd, 4.6; Loeb, 4.7; M. H. Fischer, 4.5.

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and to a lesser extent oxalic) gave curves of diminished swelling, etc. This identity, however, applies only when plotting pH against the property measured; that is, the amount of acid present may vary considerably, but, provided the pH's be identical, all monobasic acids will swell the protein to the same extent.

In this fact lies the explanation of the mystery of the "Hofmeister" or "lyotrope" series, a curious sequence of ions arranged in the order in which they affect the properties of colloids. In the compilation of this series, the factor of hydrion concentration was neglected. Provided all excess of the reacting salt is removed, the various properties of proteins, such as swelling, viscosity, osmotic pressure, etc., are in reality functions of the hydrion concentration.

All this is of great importance in considering the effect of any reagent on the hide proteins. To take a case in point: It will have been noticed that the isoelectric point for gelatin, and presumably for collagen, lies decidedly on the acid side of the point of true neutrality. The actual curve for gelatin, where swelling is plotted against pH, shows a fairly sharp rise to a maximum at about 2.4, a fall to a minimum at 4.6, and a slow gradual rise to a maximum at about 12. If a hide is in a liquor of pH 2, for example,[8] decreasing the acidity will increase the swelling until a pH of 2.4 is reached, then will decrease the swelling to a pH of 4.6. Similarly, for a hide in liquor of pH 6, increasing acidity will decrease the swelling until a pH of 4.6 is reached. And all this is on the acid side of the neutral point. The importance of the swelling curve in relation to pH is then obvious in tan liquors, the manufacture of synthetic tannins, and the like.

Constituents of Hide

The individual constituents of hide may be divided into proteins, fats, and mineral salts.

The mineral salts consist of phosphates and aluminates in very small quantity associated with keratin in the epidermis and of small quantities of various mineral substances, chiefly sodium and potassium chlorides, calcium and magnesium phosphates, in the blood. In the latter also occurs hematin, a highly complex organic iron salt. Generally speaking, the mineral constituents of skin are negligible.

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The proteins are mainly scleroproteins or albuminoids (*i. e.*, miscellaneous proteins not allotted to any group), but also include some albumins and globulins.

Collagen—Of the proteins, the most important to the tanner is collagen, which forms the constituents of the white fibers of the corium. It contains carbon, hydrogen, nitrogen, oxygen, and perhaps a little sulfur. Analyses vary slightly, indicating that conceivably there may be more than one collagen, but the difficulty of obtaining a pure product probably explains the variations.

In fresh hide the white collagenous fibers are somewhat swollen and hydrated. The normal method of purification, which is used in practice, consists in washing, liming, unhairing, deliming, bating, and scudding, thus removing keratins, mucins, and elastins. Such a collagen is hide powder.

As to structure, it has been argued that collagen has a ring formation, since trypsin will not act on it unless it be previously swollen with acid or alkali, or treated with pepsin. On the other hand, many synthetic polypeptides cannot be hydrolyzed by trypsin, but still possess an open chain structure.

From the fact that boiling collagen with water hydrolyzes it to gelatin, and from the general similarity between the two, it is commonly supposed that collagen is an anhydride of gelatin.[5] Furthermore, gelatin heated above 100° is gradually converted into an insoluble substance which, apart from its lack of fibrous structure, closely resembles collagen. Since it is impossible to obtain gelatin again from this by mere boiling,[6] this argument is of doubtful value. It is known that hide dried at 60° for some hours cannot be softened back, and this is similar to the effect of heat on gelatin. Merely as a suggestion, this hardening on heating may be similar in origin to the coagulation of egg albumen. Analysis does not help in determining the question; the similarity in the figures is great. Collagen has a slightly higher carbon content than gelatin, but is lower in nitrogen, the differences being too small for definite conclusions. On the other hand, collagen gives positive Millon and xanthoproteic tests, indicating the presence of tyrosine and phenylalanine, tests which are negative or only very slightly positive with gelatin.

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Collagen forms salts, just as gelatin does, and we may have, for instance, collagen chloride and lime collagenate, depending on the pH's of the solutions employed. There can be but little doubt that collagen is appreciably changed during the earlier processes of leather manufacture, and hence the collagen of fresh and delimed hide is not necessarily identical. The slow hydrolysis of collagen, by alkalies or acids, has not been studied.

The formation of salts by collagen is of importance in the theory of tanning. There is now no reason for doubting the formation of collagen tannates, collagen chromates, or chromium collagenates, as the case may be. But this is not to say that one single theory will explain every type of tannage. So many substances can be used to tan leather that no one explanation can at present cover all. Further, Shorter[7] found that the electrical reactions of skin varied according to tannage. With raw hide and wool rubbed together, the hide had a negative and the wool a positive charge; the same applied to oil leather and wool, but with vegetable tanned leather and wool, the wool had a negative and the leather a positive charge.

Elastin—The most stable protein of hide is elastin, found in the yellow elastic fibers. It also occurs in many tendons of the body, including the *ligamentum nuchae*, the tendon at the back of the ox's head, and it is the elastin from these sources rather than that of the skin which has been most studied. It has extraordinary elastic properties. The writer found that a piece of *ligamentum nuchae* of about 1 cm. square section gave on a testing machine an extension of 150 per cent before breaking, the strain being too small to measure (*i. e.*, less than 5 pounds). Elastin is not completely dissolved on boiling with water, is scarcely attacked by acetic acid or cold or hot 1 per cent alkali, and apparently does not combine with tannin or chrome. The writer found that *ligamentum nuchae* is, however, slowly digested by lime solutions, though this may be due to bacteria. It is very slightly attacked by pepsin, but more readily by trypsin, especially if previously boiled, or treated with acids or alcohol. The previous treatment of pelts with alkaline solutions may affect the elastin so as to render it less resistant to trypsin. It can be separated from hide by merely boiling after unhairing, the scutch

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remaining consisting of elastin, possibly somewhat changed in process.

Keratin—Keratins occur in the epidermis, hair, hair sheaths, walls of sudoriferous and sebaceous glands, and cell walls in the blood. Usually they are classed as "old" or "young" keratin, the latter forming the basal layers of the epidermis. The chief difference is that young keratin is more easily hydrolyzed than is old keratin by the action of proteoclastic enzymes (*e. g.*, trypsin and pepsin) or dilute alkali. Both are insoluble in water, except on boiling under pressure; they are hydrolyzed by concentrated alkali or sodium sulfide solutions. Since dilute acids may be used to unhair,[8] possibly young keratin is soluble therein.

Mucin—Mucins occur in the so-called "coriin" or cementing substance. Procter regards this as some substance "nearly identical with, but somewhat more soluble than that of the fibrils themselves."[9] It is easily soluble in dilute acid or alkali. Van Lier[10] found it was rather a mucoid, and was usually contaminated with nucleoproteins. By repeated extraction of pelt with half saturated lime water, he found no more could be obtained and therefore claimed that it is not a hydrolytic decomposition product of collagen. It is precipitated by five per cent acetic acid, but is soluble in excess; the precipitate consists of a mass of stringy fibers. It is soluble in one to two per cent hydrochloric acid, and, on boiling some time, reduces Fehling solution. Ox, horse, and calf mucoid appear identical, but they differ from mucoid obtained from tendons. Eitner[11] states that it is rendered less soluble on drying at a high temperature. Long liming will obviously open up the fibers by dissolving the coriin.

The blood and lymph in skin are responsible for the presence of serum-albumin and globulin, fibrin, and keratins of the cell walls. Albumin combines with tannin, but is usually removed by soaking and liming.

Fats—The fats of the fat cells consist chiefly of lecithins and cholesterols, *i. e.*, mixed triglycerides, in which a complex phosphoric acid-choline radical replaces one hydroxyl, and alcohols. In certain sebaceous glands cetyl and octodecyl alcohols have been reported. Unfortunately our knowledge of the skin fats is still very limited, and other bodies may also be present in the fat cells.

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Much yet remains to be done before the chemistry of skin can be considered to be thoroughly understood, but though progress has been slow in the past, each forward step materially widens the path for those who follow. In any case, it is only through a sounder knowledge of the basic raw material that the art and science of leather manufacture can hope to make progress.

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INFLUENCE OF SODIUM CHLORIDE, SODIUM SULFATE AND SUCROSE ON THE COMBINATION OF CHROMIC ION WITH HIDE SUBSTANCE*

By Arthur W. Thomas and Stuart B. Foster

Continuation of the authors' work offers evidence that the retarding action of neutral salts in chrome tanning is due to the formation of addition compounds, with hydration as a secondary cause.

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*Reprinted from *J. Ind. and Eng. Chem.*, 14, 132 (1922).

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The significance of the presence of neutral salts in chrome liquors was first shown by Wilson and Kern,[1] and several studies of their effects have been published from this laboratory.[2] Recently Wilson and Kern[3] made a further investigation of the question and suggested as an hypothesis that the retarding action on the chrome tanning might be due to hydration by the added salt, resulting in an actual increase in the concentration of chromic ion. Since Miss Baldwin[4] had found that increase in concentration of a chrome liquor over 16 g. Cr_2O_3 per liter resulted in a diminution of the amount of chromium fixed by hide substance, this hypothesis appeared reasonable.

If hydration did take place, the concentration of hydrogen ion should be increased as well as that of the chrome. That this was actually the case with chlorides was shown by Thomas and Baldwin,[5] but at the same time they demonstrated that sulfates lower the hydrogen-ion concentration of acid solutions, as measured by the hydrogen electrode. Since Wilson and Kern found that sodium sulfate decreased the fixation of chrome, just as sodium chloride and other chlorides did, they were obliged to admit another possible factor, namely, the formation of addition compounds between the chromium salt and added sulfate as well as between the acid present and added sulfate.

With the view of approaching a solution of this question the following experiments were carried out. In addition to sodium chloride and sulfate, the former raising the C_{H^+} and the latter lowering it, sucrose was selected as a hydrating nonelectrolyte since H. C. Jones[6] has shown that it hydrates considerably in aqueous solution. Inasmuch as Thomas and Kelly[7] had shown that in a period of 48 hours' contact the maximum combination of chrome with hide substance was effected by a chrome liquor containing 15.5 g. Cr_2O_3 per liter, three sets of liquors were selected, one containing 15.5 g. Cr_2O_3 per liter, and two others 3 g. and 100 g. Cr_2O_3 per liter.

[1] *J. A. L. C. A.*, 12 (1917), 445.
[2] *Ibid.*, 13 (1918), 248; 14 (1919), 10; *J. A. C. S.*, 41 (1919); 1981.
[3] *J. A. L. C. A.*, 15 (1920), 273.
[4] *Ibid*, 14 (1919), 433.
[5] *J. A. C. S.*, 41 (1919), 1981.
[6] *Carnegie Inst. Publ.*, 60 (1907).
[7] THIS JOURNAL, 13 (1921), 31.

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Materials and Technic

1920 and 1921 American Standard Hide Powder served as the source of hide substance. The chrome liquors were prepared by dilution of pure concentrated liquors made by reduction of chemically pure sodium dichromate with sulfurous acid, as described by Thomas and Kelly.[8]

Portions of hide powder equal to 5 g. of absolutely dry substance were covered with 50 cc. of distilled water in bottles, and allowed to stand over night, when the salts or sugar to give the desired concentrations were added. Finally 150 cc. of chrome liquor were added, of such a concentration that if it were diluted to 200 cc., it would contain 3, 15.5 or 100 g. Cr_2O_3 per liter. The mixtures were rotated in a tumbling machine for 48 hours, filtered through muslin bags, and washed well with tap water and three times with 200 cc. portions of distilled water. The powder was air-dried at 30° C., then at 100° C., and finally allowed to come to equilibrium with atmospheric humidity. Moisture, nitrogen, and chromium were determined. Multiplication of the per cent nitrogen by 5.614 gave per cent hide substance. All figures in the tables are on the moisture-free basis.

TABLE I—(Liquor Contained 3 G. Cr_2O_3 Per Liter)

Concentration of salt *M* (NaCl)	Protein per cent	Cr_2O_3 per cent	Mg. Cr_2O_3 per g. hide substance
0	83.75	4.44	53
0.5	88.01	3.62	41
1	90.03	3.16	35
2	90.37	3.45	38
3	88.05	3.75	43
4	87.58	4.19	48
(Na_2SO_4)			
0.5	90.71	4.35	48
1	91.27	3.19	35
2	93.12	2.13	23
3	91.82	2.11	23

Measurements of the hydrogen ion concentration of the liquors belonging to Table II verified the contrasting effects of sodium chloride and of sodium sulfate previously reported from this laboratory.

[8] *J. A. L. C. A.*, 15 (1920), 665.

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TABLE II—(15.5 G. Cr_2O_3 PER LITER)

Concentration of salt M (NaCl)	Protein per cent	Cr_2O_3 per cent	Mg. Cr_2O_3 per g. hide substance
0	77.92	9.01	116
0.5	79.18	7.59	96
1	81.27	5.93	73
2	82.86	5.26	63
3	84.38	5.90	70
4	83.93	5.85	70
(Na_2SO_4)			
0.5	81.07	6.58	81
1	84.32	5.29	63
2	83.48	5.76	69
3	85.44	4.36	51

TABLE III—(100 G. Cr_2O_3 PER LITER)

Concentration of salt M (NaCl)	Protein per cent	Cr_2O_3 per cent	Mg. Cr_2O_3 per g. hide substance
0	75.57	7.70	101
0.5	80.78	6.17	76
1	82.13	6.15	75
2	82.42	6.35	77
3	81.23	6.35	79
4	79.10	6.77	86
(Na_2SO_4)			
0.5	80.17	6.62	83
1	81.07	6.01	74
2	77.42	6.11	79
3	78.08	6.87	88

The results are plotted in Figure 1. The curves representing the effect of sodium chloride all proceed to a minimum and show

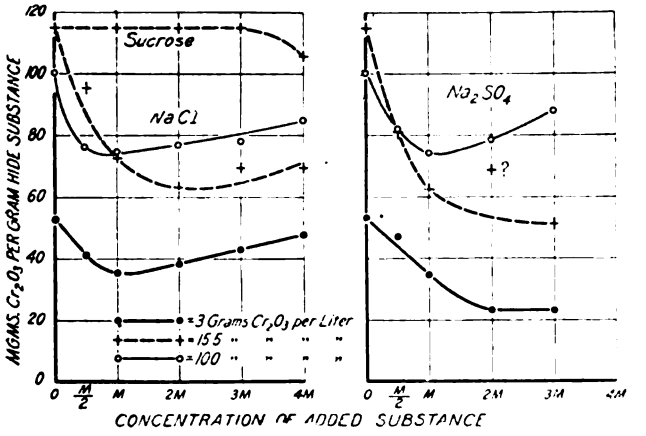

Fig. 1

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an upward trend similar to the results Wilson and Kern found with magnesium chloride. In all cases sodium sulfate shows greater inhibiting action than sodium chloride and a minimum with upward slope is obtained only where the liquor is very concentrated. Contrasted to the effect of the electrolytes, we find that sucrose apparently has no effect except at 4 *M* concentration.

TABLE IV—(15.5 G. Cr_2O_3 PER LITER)

Concentration of sucrose *M*	Protein per cent	Cr_2O_3 per cent	Mg. Cr_2O_3 per g. hide substance
0	77.47	8.92	115
1	74.76	8.59	115
2	74.72	8.59	115
3	74.83	8.60	115
4	76.74[1]	8.13	106

[1] This sample appeared to be scorched in spots after drying at 100° C.

TABLE V—(LIQUORS CONTAINED 15.5 G. Cr_2O_3 PER LITER)

Concentration of salt *M*	Log C_H + of original liquor	Log C_H + of filtrate
0	—2.78	—2.90
1	—2.54	—2.67
2	—2.39	—2.43
3	—2.20	—2.33
4	—2.10	—2.20
(Na_2SO_4)		
0	—2.80	—2.85
1	—2.91	—2.92
2	—2.91	—3.07
3	—2.67	—3.01

INTERPRETATION OF RESULTS

Since sucrose hydrates in aqueous solution, the inhibition of the fixation of chrome by the lower concentrations of sodium chloride and of sodium sulfate does not appear to be due to hydration. The writers believe that, as Wilson and Kern suggested for sulfates, sodium chloride, as well as the sulfate, forms addition compounds with the constituents of chrome liquor, rendering them less dissociated and consequently less active in combining with the proteins of hide substance. This is like the influence of sodium chloride in inhibiting the adsorption of mercuric chloride by charcoal, which Rona and Michaelis[9] point out is similar to the decrease in toxicity of mercuric chloride in the presence of sodium chloride. They ascribe such effect to the formation of the complex ions $HgCl_3^-$ and $HgCl_4^=$.

[9] *Biochem. Z.*, 97 (1919), 85.

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Upon increasing the concentration of salt the hydration effects a virtual concentration of the chrome to such an extent that the retarding action of the addition compound formation is counterbalanced somewhat by the activity of the high chrome concentration, and the curves slope upward. Sodium sulfate does not show the upward slope because, first, owing to mass action it can drive back the ionization of chromic sulfate which represses the activity, as well as causing addition-compound formation, and, second according to the results of H. C. Jones, it does not hydrate to a large extent. The upward trend with sodium sulfate is shown only where the liquor is very concentrated at the beginning. That the effect of hydration is secondary to addition compound formation is illustrated by sucrose. While it hydrates in aqueous solution, it has no retarding effect on the fixation of chrome. It would seem that since it does not retard the action of the chrome, it must not form the addition compounds, except of concentrations over 3 *M*. The 4 *M* value shows a retardation which we ascribe to a different chemical mechanism. The effect of compounds with several hydroxy groups in forming soluble un-ionizable complexes with the metals, such as tartrate with copper, mannite and glycerol with iron, etc., is well known. The 4 *M* sucrose chrome solution was thick and sirupy in consistency and it seems plausible that a similar compound of chromium and sucrose was formed.

ACKNOWLEDGMENT

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ABSTRACTS

Tannin Analysis and the Conference. By H. R. PROCTER. *J. S. T. C.*, 5, 219 (1921). Some suggestions for investigations by Committees of the S. L. T. C., on the method of tannin analysis, with a view to its improvement, which are as follows:—(1) Method of filtration: (a) Question of "true insolubles," etc. (b) Optical clearness of filtrates. (2) Effect of acidity (p^H) of solutions on: (a) amount of insolubles, (b) amount of non-tannins. (3) Colour measurement. (4) Question of washing hide powder after detannisation. (5) Manufacture of hide powder.

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Experiments on Imbibition. By A. G. Brotman. *J. S. L. T. C.*, **5**, 226 (1921). Pure air-dry gelatin when immersed in pure water will imbibe water to a certain maximum amount—the ratio imbibed water/gelatin varying with the kind of gelatin employed. The time required for maximum imbibition is for the "leaf" variety of gelatin about 24 hours. When such a gel, which has apparently imbibed the maximum amount of water, is melted by immersing in a water bath at 80° C. for 2 minutes and is allowed to set and re-immersed in water is capable of imbibing more water. There again appears to be a maximum value for the ratio, imbibed water/gelatin.

Dispersion apparently effects a distribution between the gelatin and water in the gel, which differs from that existing in the gelatin which has simply imbibed a maximum amount of water.

The imbibing capacity of a sample of gelatin can be increased by dispersion to a very considerable extent. The capacity for imbibition of water of a gel depends on the quantity of gelatin it contains and on the distribution of the gelatin in the gel, *i. e.*, on the gel structure.

Determination of Optimum Temperature and State of Sub-division for Maximum Extraction of Tannin from Goran Bark. By B. B. Dhavale and S. R. Das. *J. S. L. T. C.*, **5**, 229 (1921). The optimum temperature for the extraction of goran bark (*Ceriops Roxburghiana*) varies with the sub-division of the particles under extraction. The finer the size of the particles, the lower is the optimum temperature. Four mesh and 10 mesh sub-divisions have a common optimum temperature at 55°-60° C.; the 20 mesh size has 50°-55° C. as its optimum temperature, while that for the 60 mesh is 45°-50° C.

The quantity as well as the quality of tannin extracted at the respective temperature ranges vary from one sub-division to the other. At its optimum temperature the 4 mesh sub-division yields 25.39 per cent, the 10 mesh 28.49 per cent, the 20 mesh 25.95 per cent, and the 60 mesh 34.79 per cent of tannin. Although the 60 mesh sub-division yields the greatest quantity and best quality of tannin at the lowest temperature, it can not be recommended as a suitable size for extraction as it would bring in trouble due to clogging during operation. Out of the remaining three sub-divisions the 10 mesh one allows the highest amount of tannin to be extracted consistently with a high ratio of tans to non-tans and seems, therefore, to be the best suited for extract manufacturers.

Swelling of Hide Powder—I. By E. C. Porter. *J. S. L. T. C.*, **5**, 259 (1921). A study has been made of the swelling of hide powder in buffer solutions ranging in p^H from 1 to 12.5. There appears to be a maximum of swelling at $p^H = 2.4$, a minimum at $p^H = 4.8$, and a second maximum, probably, at about $p^H = 12.5$. Neutral salts were kept, as far as possible, at constant concentration.

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The Procter-Wilson Theory as a Working Tool. Its Application to Sewage Disposal. By J. A. Wilson. *J. S. L. T. C.*, **5**. 268 (1921), The Procter-Wilson theory of the swelling of protein jellies in acids has been applied to the filtration of sludge from the sewage of the city of Milwaukee. The addition of acid materially altered the rate of filtration and at the optimum point (p^H of filtrate = 3.2) the time required was reduced to one-fourth. Still better results were obtained by the addition of aluminum sulphate and then adjusting the p^H to 4.3. The time then required for filtration is one-eighth of that required by the untreated sludge.

Report of Tanning Analysis Committee (S. L. T. C.) on Washing of Hide Powder. *J. S. L. T. C.*, **5**, 274 (1921). In the washing of hide powder distilled water only may be used. The use of tap water leads to great irregularities in tannin analysis.

Note on the Microscopical Analysis of Sumac. By W. R. Atkin and R. H. Marriott. *J. S. L T. C.*, **5**, 275 (1921). Polarised light is applied to the microscopical analysis of sumach. Photomicrographs are given showing the characteristic appearances of *Rhus coriaria, Tamarix Africana, Pistacia lentiscus* and *Colpoon compressa.* Claim is made that the method gives more definite and quicker results than the ordinary microscopical routine.

The Removal of Elastin During Bating. By R. H. Marriott. *J. S. L. T. C.*, **5**, 280 (1921). The statement that one essential part of bating is the removal of elastin is criticised. Experiments described show that whilst elastin is digested by an enzyme bate, this removal is not a fundamental of the process. The solution of cementing substance is suggested as one of the essential features of true bating. The structure of elastin is discussed with regard to its lack of optical activity under polarised light.

Some Indian Vegetable Tannins. By W. R. Atkin and K. H. Hassan. *J. S. L. T. C.*, **5**, 347 (1921). Twelve Indian tanning materials have been analysed by the official method of the *S. L. T. C.* and also qualitatively according to Stiasny's scheme. The results are given in tables.

Water Soluble Matter in Vegetable Tanned Hide Bellies. By W. J. Chater and D. Woodroffe. *J. S. L. T. C.*, **5**, 359 (1921). It was not found possible to establish any definite connection between the water-soluble content of various leathers and their permeability to water. However, when strips of leather were suspended with their ends in water, it was found that the leathers with the highest water-soluble content allowed the least capillary rise of water and *vice versa.*

The Formaldehyde-Gelatin Combination. By A. G. Brotman. *J. S. L. T. C.*, **5**, 363 (1921). The amount of formaldehyde fixed by gelatin is shown to be a function of the concentration of the jelly—a weak jelly fixing more formaldehyde than one more concentrated when

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conditions are such that equal quantities of water, formaldehyde and gelatin are present, although with the weakest gel there is the greatest volume of jelly and the smallest volume of external solution.

Notes on the Mallet Bark. By H. Salt. *J. S. L. T. C.*, **5**, 366 (1921). Mallet bark is a typical product of Western Australian forests. Several distinct species are classified, stripped and sold as "Mallet":— Mallet (*Eucalyptus occidentalis, astringens*), Silver Mallet (*E. falcata*), Blue Leaf Mallet (*E. redunca, oxymitra*) and Swamp Mallet (*E. spathulata*). All of these are valuable tanning materials.

Tannins and Allied Substances—VIII. The Tannin of the Wood of the Chestnut (*Castanea vesca*). By K. Freudenberg and H. Walpuski. *Ber.* **45**, 1695 (1921) through *J. S. C. I.* **40**, 781A (1921). The isolation of the crude tannin from the wood is described in detail, the total yield being more than 5 per cent of the weight of the wood. Hydrolysis with dilute sulphuric acid gives a little quercetin, traces of gallic acid, 2 per cent of sugar (chiefly dextrose), and 15-20 per cent of ellagic acid all of which are present initially in the combined form; simultaneously, however, the tannin is itself extensively decomposed. It appears stable towards emulsin but is slowly hydrolysed by relatively large amounts of *aspergillus* tannase, finally giving a product from which less than 3 per cent of ellagic acid is liberated by treatment with dilute sulphuric acid; simultaneously the quercetin component is hydrolysed whilst traces of gallic acid and small amounts of sugar, chiefly dextrose, are obtained. The purified tannin is a yellowish-red, strongly acidic substance which comprises more than half of the original crude product. It shows the usual reactions of tannins. It is not affected further by tannase and is not decomposed into simpler constituents by other hydrolysing agents. It does not appear to be an ester tannin or a catechin and is most closely allied to the product derived from the native oak.

Dynamics of the Formation of Gelatin from Ossein. By A. B. Mannnig and S. B. Schryver. *Biochem J.*, **15**, 523 (1921) through *J. S. C. I.*, **40**, 742A (1921). Ossein was prepared from crushed bones, extracted with alcohol, ether, and cold acid. The rate of extraction of gelatin from this by water at 100° and 90° C. was determined; although it depends on the size of the fragments there is no true surface effect. Owing to porosity the actual surface is independent of the extent of crushing, and the rate of extraction of gelatin is conditioned by its diffusion through the pores.

A New Leather-Grease. By W. Fahrion. *Chem. Umschau*, **28**, 244 (1921), through *J. S. C. I.*, **40**, 859A (1921). Mineral oils are not suitable for fat-liquoring leather, as the latter becomes hard and brittle. The addition of calcium soap to the mineral oil overcomes this disadvantage. In order to make the mixture emulsify with water and so suitable for treating wet leathers neutral fat or fatty acids must be added. In a patented process a mixture of fatty acids and mineral oil is heated to

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110° C. and the calculated quantity of calcium hydroxide gradually stirred in. After allowing the mixture to stand, it is transferred warm to a mixing pan, warm water added, and the whole stirred until cold. The product has a very smooth texture and the appearance of dégras. A grease containing 8 per cent of calcium soap, 8 per cent of neutral fat, 64 per cent of mineral oil, and 20 per cent of water has been found quite satisfactory. It is also applicable to chrome leathers under certain conditions. It is considerably cheaper than the animal fats in use up to the present.

Analysis of Sodium Sulfide Crystals. By J. A. Wyler. *Col. Tr. Jour.*, 9, 159 (1921). *Sodium Sulfide*: — Weigh a 50 gram sample of the crystals as rapidly as possible, dissolve in water and transfer to a liter flask. Dilute to the mark, take 100 cc. and dilute to 500 cc. in a graduated flask. A 100 cc. portion of the latter solution is run into a 600 cc. beaker containing 100 cc. of water and 5 cc. acetic acid, while at the same time N/10 iodine is run in from a burette. The sulfide is run in at such a rate as to be in slight excess at all times. When all of the sulfide has been run in, starch indicator is added and the iodine is slowly added until a blue color appears. It is important to have the tip of the pipette containing the sulfide under the surface of the solution in the beaker. Sodium sulfide is obtained by subtracting from the amount of iodine solution used in this titration, the amount required for thiosulfate present, 1 cc. N/10 iodine = 0.0039 gram Na_2S or 0.0120 gram $Na_2S.9H_2O$.

Sodium Thiosulfate.—Weight 10 grams of the sample, dissolve in 300 cc. of water, and add normal hydrochloric acid from a burette until the solution is neutral to Methyl Orange. Due to the action of the hydrogen sulfide on the indicator it is difficult to get a close end-point, but it is safe to add about 2 drops of the acid in excess if this acidity is promptly neutralized with normal caustic soda. Now add 5 cc. of 25 per cent magnesium chloride solution and boil vigorously to expel the last traces of hydrogen sulfide. With experience it will be possible to dispense with the addition of magnesium chloride, as it is only a matter of experience to be able to get a good end-point with the acid titration. On boiling the vapor should be tested with lead acetate paper to ascertain when all the hydrogen sulfide has been expelled. All hydrogen sulfide having been driven out, the mixture is diluted to about 200 cc. with cold water and cooled to room temperature. A slight precipitate of magnesium hydrate will usually be present at this stage. Now add a few drops of Methyl Orange indicator and add normal hydrochloric acid slowly with stirring until the solution is barely acid. The solution is now titrated with N/10 iodine, using a starch indicator. This reading gives the sodium thiosulfate and sulfite. Since the sulfite is usually absent, or present only in small amounts, this reading is considered the thiosulfate titration. 1 cc. N/10 iodine equals 0.0158 gram of sodium thiosulfate ($Na_2S_2O_3$).

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Sodium Carbonate and Sodium Sulfhydrate.—Ten grams of the sample are dissolved in 200 cc. of water (hot), and 25 cc. of a 10 per cent barium chloride solution are added. The mixture is covered, allowed to stand on the steam plate for five minutes, paper pulp added and then filtered with suction. The precipitate is carefully washed with hot water, not allowing the filter to be sucked dry. The washed residue is transferred to a 600 cc. beaker; 25 cc. of water added and then an excess of normal hydrochloric acid added from a burette. Now add 200 cc. of hot water, stir to allow the acid to attack the barium carbonate, cool, add a few drops of Methyl Orange and titrate the excess of acid with normal caustic soda. The acid consumed corresponds to the carbonate.

One cc. normal HCl equals 0.05300 gm. of sodium carbonate (Na_2CO_3).

The filtrate from the carbonate precipitation is transferred to a liter flask and an excess of a 1½ per cent cadmium sulfate solution (neutral) added with shaking. Heat on the steam bath for one-half hour, add paper pulp and filter with suction. Evaporate the filtrate to 200 cc. volume and titrate the free acid with normal caustic soda using Methyl Orange indicator

One cc. normal NaOH equals 0.05607 gm. of sodium sulfhydrate (NaSH).

Methods for determining chlorine, total sulfur, total sodium and iron and aluminum oxides are also given.

Effect of Change of Acidity upon the Rate of Diffusion of Tan Liquor into Gelatin Jelly. By J. A. Wilson and E. J. Kern. *J. Ind. and Eng. Chem.*, **14**, 45 (1921). Five per cent dispersions of gelatin were prepared containing 0.1 per cent ferric chloride, tartaric acid sufficient to give an original p^H value of 2.5, and sodium hydroxide sufficient to give a series of dispersion with a range of p^H values from 2.5 to 11.0. Portions of a gambier and a quebracho solution were treated in the same manner with tartaric acid and sodium hydroxide to give a series of solutions with p^H values corresponding to the series of jellies The gelatin dispersions were allowed to set in test tubes and a given volume of tan liquor having a corresponding p^H value was poured on each . These were kept in an ice box and examined at intervals for 96 hours. At the end of 96 hours the extent of penetration as measured by the iron coloration was measured and the results were plotted against the p^H values of the solution. Gambier begins to penetrate at a p^H value of 3.0, reaches its maximum of 18 mm. at $p^H = 6.0$, and at $p^H = 11.0$ it has fallen again to 10 mm. Quebracho begins to penetrate at $p^H = 4.7$ and reaches a maximum of 12 mm. between p^H values of 10.0 and 11.0.

G. W. S.

Physiological and Historical Studies on Flayed Skins. By A. Seymour-Jones. *Chem. and Met. Eng.*, **25**, Dec. 7, 1921. The skin consists of two main divisions, the epidermis and the corium. The epidermis is entirely composed of keratins and their derivatives. The corium con-

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sists principally of collagen, keratins, elastin and fats. After removal of the epidermis and hair and "*the flesh*" which is the *panniculus adiposus*, or loose connective tissue joining the skin to the animals body and which forms the flaying line, the corium or "*pelt*" is obtained. The author divides the corium into four parts:— (1) The grain membrane which must be considered as much a part of the corium as it is of the epidermis, being partly keratinous and partly collagenous and containing a comparatively large proportion of elastin. It yields very little gelatin on boiling. (2) The *Cutis Minor* is the *cutis vera* of the human skin histologists but the author regards the entire corium as the *cutis vera* or true skin. The *cutis minor* is composed of white collagenous fibers, yellow elastic fibers, *erector pili*, or hair erecting muscles, nerve fibers, sudoriferous ducts, blood capillaries and hairs with their accompanying epidermic follicles. It makes up from 5 to 20 per cent of the entire corium. (3) The *Stratum Adiposum* which is mainly composed of fat cells. (4) The *Cutis Major* is composed of large, thick white fibers, built up of numerous fibrils, traveling in every conceivable direction. This layer is collagenous and contains blood vessels and nerve fibers. It is devoid of elastic fibers.

The elastic fibers are under tension and their function in the *cutis minor* is conceived as for keeping this layer under tension so that it may act as a resilent cushion and allow of free circulation of lymph. This conception is verified by simply cutting through the *cutis minor* layer, as is done in making a grain split when some of the elastic fibers are severed and the area of the grain split becomes greater than that of the flesh split. In digesting the elastic fibers as in bating with trypsin the extensibility of the grain is greater. The use of trypsin as a bate digests the elastic fibers but it is a question if this is the only function of bating. Our forefathers employed what has been called the "river process," the skins being left in a soft water running stream until they were soft and flaccid. Also the bran drench is used alone as a bate with great success.

G. W. S.

Report of the French Committee on Leather Analysis. By M. P. Chambard, *Chairman*. *J. S. L. T. C.*, **5**, 313-22 (1921); *Le Cuir*, **10**, 418-23 (1921). *Sampling.*— A French hide tanned for six months, using sulphited quebracho, chestnut and oak bark, was selected. A side of this was ruled off into rectangular pieces and samples taken at the intersection of the lines were analyzed. The results obtained show an area in the butt with a maximum of 43 per cent hide substance which decreases rather regularly to 35 per cent towards the belly and shoulder. It also shows a large zone at the junction of butt and shoulder of nearly constant composition, 35.5 to 36.0 per cent and furthermore, this holds true in a direction perpendicular to the back bone line so that a sample taken in this direction and in this zone will have a constant composition. This has been confirmed by the experience of the chairman, who has not found a difference of more than 1 per cent in hide substance in samples

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taken in this manner from sides chosen at random out of the same lot of leather, it being understood that other factors such as weight, origin and so on were equal. This section is therefore considered the best for samples of constant, but not necessarily average, composition. The piece should be 5 cm. wide and cut between the shoulder and butt. Six cm. from each end of this strip should be discarded.

Preparation of Sample—Fifteen to twenty grams are planed off and bottled for moisture, ash and water solubles; about 3 grams from the central part of the sample are cut into regular sections or slices for nitrogen determination.

Moisture—Drying in a hot air oven at 105-110° until constant in weight, which generally requires three hours, is proposed. A special, wide shallow dish with ground cover is recommended to prevent re-absorption of moisture by the dried leather. The top has a very small hole in the center and is put on the dishes before they are removed from the oven. A charge of 5 grams is used.

Water Solubles—The method studied is the one usually employed in France, and is easy to define and simple in details. The quantity of water should be very large in relation to the weight of the sample, yet the extract should be of sufficient strength to permit the use of a 50 cc. aliquot. The previously chosen quantities of 250 cc. of water and 5 grams of leather are quite satisfactory. The extraction may be made either with agitation in which case it is complete in four hours so that the time has been fixed at five hours; or without agitation in an apparatus described [see This JOURNAL **16**, 383-84 (1921)] which requires 14 hours and consequently for convenience the time has been fixed for overnight or 16 hours. Results at the same temperature with and without agitation show good agreement. The effect of temperature over a range of 11 to 40° C. was studied on two leathers, one of medium tannage and one of rapid tannage, using with both, sulphited quebracho and chestnut. These leathers gave a quite distinct maximum at 18 to 21° C. It must be noted that these leathers were tanned with the same materials and that with other tannins different results might be obtained. The results show, however, the need of defining the temperature of extraction.

Hide Substance—The present Kjeldahl method precribes 0.7 gram sample which is considered too small to give a representative charge. On the other hand digestion and oxidation, with permanganate, of larger quantities is difficult. It has been found that the method of digestion usually employed for silk gives the best results and allows of rapid and easy digestion of large charges up to 5 grams. The ammonia is collected in 0.2 N sulphuric as the color change with cochineal is sharper than with 0.1 N acid. Results given on white hide and leather are extremely constant.

Proposed Methods for Analysis of Leather: *Sampling*—For sides, determine the total length from tail to ear and from the latter point mark off one-third of the length along the backbone line and drop a per-

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pendicular. Along this perpendicular take a strip 5 cm. wide; discard 6 cm. from each end and the remainder will constitute the sample, of about 80 grams.

For butts (bends), a similar strip is taken from the edge towards the shoulder.

For shoulders, a similar strip 3 cm. wide is taken from the edge from which the butt was cut.

For bellies, a strip 3 cm. wide is cut from the edge common to the butt and belly, and one-fourth from each end of the strip is rejected

The sample is to be prepared by planing, except 3 to 6 grams for hide substance determination, which are to be prepared by slicing with a knife, each slice 1 to 2 mm. thick and representing a vertical section of the leather.

Moisture—Five grams of planed leather are dried in a flat dish or special container, previously described, in a hot air oven at 105–110° C. until constant in weight (3 hours).

Water Solubles—For extraction with agitation, 5 grams of planed leather are put in a 400 cc. flask with 250 cc. of distilled water at ordinary temperature and shaken for 5 hours. Without agitation, 5 grams are placed in a metallic basket, in the apparatus already described, with 250 cc. of water and left at the selected temperature for 16 hours. The water should cover the leather to the extent of 1 to 2 mm. The extract is filtered through a 16 cm. paper without the use of kaolin, the first 50 cc. are rejected, from the rest of the filtrate 50 cc. are dried to constant weight (3 hours) in a dryer at 98–100° C.

Hide Substance—In a 200 to 300 cc. Kjeldahl flask, 2.8 grams of sliced leather are digested with 25 cc. of 66° sulphuric acid, 7 grams of dry potassium sulphate or 10 grams of dry potassium bisulphate, and 0.5 gram of anhydrous copper sulphate. The mixture is digested for 1 to 2 hours or until pure green when hot and blue when cold The solution is transferred to a 1000 cc. flask with 300 cc. of water and made slightly alkaline with sodium hydroxide. It is then distilled, 200 cc. of distillate being collected in 100 cc. of 0.2 N sulphuric Titration is made with 0.2 N sodium hydroxide using a suitable indicator such as cochineal. The factor 5.62 is used to convert to hide substance.

Mineral Matter—Five grams of planed leather are ashed in a platinum dish at a dull red, until a white ash is obtained. Fusion of the ash by too high a temperature should be avoided.

Fats—Five grams of planed leather are extracted in a Soxhlet with petroleum ether. The excess of solvent is distilled off and the extract dried and weighed.

R. W. F.

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Useful Tannery Notes. By A. T. Hough. *Le Cuir*, 10, 465-68 (1921.) Sulphonated castor oil should be clear, light yellow and but slightly viscous according to its strength. Cloudy oils may be of good quality but in general are not as good as clear ones. A good oil should not have a disagreeable odor but rather one faintly suggestive of castor oil. A sample used sometime ago had an odor of rotten eggs, was cloudy and dull gray, and left gray streaks on the leather. The oils should not have an ammoniacal odor but should be neutral or rather acid. Any free alkali is sufficient to condemn the oil, and soda is worse than ammonia, because of oxidation of the tannin, discoloration of the leather and often brittle grain. A simple practical test of the reaction of the oil can be made with litmus paper. An oil which separates on standing into two layers indicates hasty manufacture. In this case the oil is also generally cloudy. While in general such oils will not cause trouble they should be avoided as indicating poor plant operation. Certain sulphonated oils give a milky emulsion with water while others remain clear. Though the former does not necessarily indicate poor quality, the behavior with water depends upon the degree of sulphonation and careful manufacture, and as a rule those oils which remain clear are to be preferred. The usual sulphonated oils are 40 to 50 per cent in strength, that is, dry material. Ash and impurities should not exceed 4 per cent. The approximate strength of an oil may be very simply determined by mixing in a graduated cylinder 25 cc. of the sample with 25 cc. of 20 per cent sulphuric acid and 50 cc. of saturated common salt solution. After standing overnight the volume of the oil on top is read

Acid deliming of hides may be very readily and safely controlled by periodic testing of the deliming bath with methyl red, adding acid to the bath whenever the indicator shows it is alkaline. Methyl red is a particularly suitable indicator as its color range denotes an acidity which will not produce excessive swelling of the hides. As the deliming proceeds the weak organic acids first added may be safely regenerated by addition of strong acids, such as hydrochloric or sulphuric, until the bath is acid to methyl red One bath should not be used for more than three lots of hides.

R. W. F.

The Development of Chestnut Extract Plants By E. Depasse. *Le Cuir*, 10, 459, 65, 485-91 (1921). In the early days of the industry, many small French extract plants were erected in the center of the chestnut area. These plants were run uneconomically as the wood was cheap and readily available. As a result the wood regions near the factories have been exhausted and the industry has already passed its zenith. At the beginning of the war practically all the plants were closed but the demands for leather made it necessary to reopen them. This was attended by many difficulties. Labor was very scarce and many of the plants had to cut and transport their wood. A good price was demanded for the wood, which added to the cost of labor and transportation made it very

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expensive. The foreign element, Spanish and Italian, with German, Austrian and Russian prisoners of war, made up the labor. It became necessary to allocate the wood and even the extract. Natural results of these conditions were efforts for more economical operation and greater yield.

Extraction is made according to preference either in open leaches; closed leaches; or in batteries of 5 and 6 and sometimes 8 or more autoclaves. The latter are generally employed. Before the war the liquors were cooled, decanted and often decolorized with blood. During the war they were not decolorized, being generally cooled and decanted.

The quality of the water is of considerable importance as affecting the yield. The water should be absolutely free of iron and lime and especially the latter. If these two bases are present it is well to completely recover all condensed warm or cold water from the plant and thus compensate for otherwise inevitable losses in tannin. Differences of 2 to 3 per cent in yield have been noted between plants where one used pure water and the other water of average hardness, both plants using the same wood with the same procedure and technical personnel. The important points in extraction are: the preparation of the wood, the time of extraction, the temperature, and the dilution and speed of circulation. In a way one condition can be compensated for by another but each one has a limit which is rather precise and narrow. The details of extraction are given with particular emphasis on the influence of pressure, temperature and discharge of autoclaves on the color, quality and yield of extract. At the head of the battery 80–85° C. should be the maximum while 125–130° C. may be used on the tail. About 16 autoclaves are worked in 24 hours and the dilution should be as great as the plant capacity will permit, from 150 to 200 liters or more per 100 kgs. of wood.

As the relation between heat production and consumption is of the utmost importance in the economical operation of an extract plant, and offers many opportunities for improvement over present practices, this is extensively dealt with. Detailed calculations of heat consumption for the various operations are given.

R. W. F.

Recovery of Acetic Acid in Evaporation of Extracts. By E. Depasse. *Le Cuir*, 10, 424-26 (1921). Several articles which have appeared on this subject seem to have ignored the technical conditions of operating French extract plants and one by G. Vié [This Journal **16**, 641 (1921)] gives the reader an entirely false view. It is not the process of recovery which should be criticised, but the manner of conducting it with lack of appreciation of the essential points of extract plant operation. The process consists in passing the steam containing the acetic acid distilling from the extract solutions into an alkaline solution under such conditions that there is a sufficient period of contact between the two, but

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without appreciable resistance to the passage of the steam, which would cause a fall in temperature and evidently reduce the efficiency of the evaporators. Excellent results have been obtained with an apparatus, a description of which can be found at the Patent Office (French). A recovery of 90–92 per cent of the quantity of acid distilled has been made. The apparatus must be designed to resist the mechanical action of boiling alkaline solutions which is considerable. As the apparatus normally is in contact only with alkaline solutions or neutralized vapors the kind of metal is of importance only from mechanical and not chemical considerations. The equipment for recovery of the acetic acid should be installed only when the evaporation work of a plant is properly conducted with sufficient capacity to perform the work required and without entrainment of tannin liquors. Normally, without recovery of acid, the installation for evaporating should fulfil certain conditions. With proper evaporation facilities the recovery of acid is simple, easily conducted and gives a good product of value.

It is a lack of judgment to expect the scrubbers to act also as safety traps for entrainment. Without traps the scrubbers or recovery apparatus operate poorly and give a poor yield. Substitution of copper for iron is a mistake, as besides being expensive, it permits of all the faults and irregularities of evaporation and recovery; removes a means of ready control, permits also entrainment or loss of tannin, does not allow of following the reaction closely enough, and gives an impure salt. Finally, other things being equal, the mechanical wear on the copper is greater than with iron and the latter withstands the alkaline solutions better. Those who have only partially substituted copper for iron have made a more serious error for these two metals in an alkaline or acid solution make a perfect cell with electrolysis and rapid wearing away as a result.

The successful and economic application of the process for the recovery of the acetic acid has been handicapped by the scant and improperly designed equipment and uneconomical operation of evaporation work in most French plants. The operations are contrary to all laws of evaporation, of economy of steam, water and so on. Evidently the recovery of acid as under normal evaporation processes is impossible. Also the criticism that the use of neutralized water would reduce the extraction yields does not hold for there are not four plants which recover their hot water. This is lost, even sometimes the first water coming from the direct condensation of the boilers. The process of recovery ought, and has fortunately been, of considerable help in improving the yield and quality of extracts. The difficulties have always been due to poorly designed and poorly conducted evaporation methods. The process has considerable more advantages than disadvantages but requires supervision.

As to the calculations of apparent yields Vié did not consider that only a part of the acid is recovered; that the sodium carbonate and

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lime are often impure to the extent of 12 to 15 per cent instead of 5 per cent and often contain 12 to 15 per cent of moisture; and finally that there are unavoidable losses of 1 to 2 per cent. In reality 100 kgs. of sodium carbonate give 105 to 110 kgs. of acetate and 100 kgs. of ordinary lime yield 120 kgs. of acetate. As to the use of lime, while it is of low cost, the installation was not designed for it. Had this been the case the acetate of lime would not have been concentrated to dryness in the concentrators for sodium acetate as from the viewpoint of evaporation there is a difference between the two salts, one of which is soluble in a small part of its water of crystallization while the other is not at all.

Reference is made to Jedlicka's letter on the subject [This JOURNAL, **16**, 700 (1921)] in which he cites the advantages of recovery as a matter of conservation and also states that the absence of acid in the extraction water does not influence the quality of the extracts. Whatever the conclusions on this last point a partial recovery of the acid can certainly be made from the final evaporations and since the acidity is highest in these concentrated liquors considerable acid can be recovered. Particularly is this so in the manufacture of dry extracts as the acid distilling off these concentrated liquors is enormous in quantity. Jedlicka speaks of entrainment as an inconvenience of the process, it is not, however, a fault of the process of recovery but of evaporation for without recovery the entrainment occurs but is not given consideration. Plants are known which recover the acetic acid without an appreciable trace of tannin in the acetate.

R. W. F.

Concerning the Recovery of Acetic Acid During Evaporation of Tanning Extracts. *Le Cuir*, **10**, 507-8 (1921). [See above ABSTRACTS]. G. Vié in reply to criticisms by E. Depasse of his statements on the recovery of acetic acid, especially as to yields, begs to refer to circulars of August 28, 1918, August 27, 1919, and March 20, 1920, sent out by the Association of extract makers and concerning the yields of sodium and calcium acetates. Depasse should recall these circulars since he was at that time in the employ of the Association. Depasse claims that 180 kgs. of sodium acetate per 100 kgs. of 95 per cent sodium carbonate is an exaggeration, and that the yield is actually 105 to 110 kgs. Vié however has observed in a plant running continuously from January 1 to 18, 1921, a yield of 1750 kgs. of 125° sodium acetate from 900 kgs. of carbonate which is a considerably greater ratio than 180 to 100. Concerning the use of lime, Vié gave a yield of about 12.5 kgs. of dry calcium acetate per 1000 kgs. of 25° extract. Depasse now claims this figure, too, exaggerated in spite of a note signed by him indicating a yield of 15 kgs. As to pretending that the use of lime is a makeshift for which the apparatus was not designed, Vié calls attention to one of the above circulars in which it is stated that "because of the difficulty in procuring sodium carbonate

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the substitution of lime has been studied and tried so that acetate of lime can be made under the same conditions as for sodium acetate. The procedure does not differ essentially from the one now used."

In reply to the above Depasse claims that the yields indicated by him were in terms of pure sodium acetate and did not include therefore water and variable impurities, often in considerable quantities With these variations in product, impurities and also losses it is evident that varying yields will be obtained. R. W. F.

Economical Industrial Manufacture of Sodium Sulphide and Sodium Thiosulphate. By H. Giusiana. *Le Cuir*, 10, 437-40 (1921). Sodium acid sulphate, the residue from the manufacture of acids, is intimately mixed with a reducing agent, such as sawdust, and heated in a muffle furnace at about 350° C., the fusing point of the acid sulphate. The sulphur dioxide given off is collected for subsequent use. The sodium sulphate formed is further reduced by heating with 30 per cent of pulverized anthracite in a single phase electric furnace with a potential of 35 to 40 volts and a current density of 4 to 5 amperes per sq. cm. of section and with one electrode in a graphite crucible. The reaction gives sodium sulphide and sulphur dioxide. The average consumption of electricity is 2 kw. hrs. per kg. of sodium sulphide. With a furnace of 500 kw., 5,000 kgs. of sulphide of 80 per cent purity can be produced a day. The latter concentration is necessary to eliminate polysulphides and carbonates. The electric furnace is more economical since in an ordinary reverberatory furnace 200 kgs. of coal are necessary to produce 100 kgs. of sulphide of 60–65 per cent purity. The reduction requires about 3 hours in the electric furnace but considerable experience is needed to tell just when to withdraw the sulphide.

To make thiosulphate from the sodium sulphide, the latter is dissolved in warm water and allowed to stand in closed vessels until impurities are deposited. Sulphur is then added to convert the monosulphide to bisulphide and gaseous sulphur dioxide collected from previous reactions passed through the solution. These processes would seem economical in view of the low price starting material, sodium acid sulphate, and use of the sulphur dioxide obtained from it in the first two reactions. Experiments at the University of Barcelona and others on a larger scale have proved satisfactory.

R. W. F.

Utilization of Horse Hides in the United States. By L. Masner. *Le Cuir*, 10, 429-37 (1921). The decided difference in the anatomical structure of the butt and front of horse hides is discussed. In the butt there is a horny layer, "spiegel," or shell which is very dense. A cut perpendicular to the surface shows that the fiber bundles are rather oblique, but very closely interwoven. A horizontal cut gives the impression of a very close sieve. The structure of the rest of the hide is normal but the grain resembles a little that of the goat. The shell or horny layer is common to all solipeds varying only in extent and form. In the mule hide the shell

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is generally larger, has a more curved outline at the tail and is of tighter structure. It is larger yet in the ass skin and extends over the entire surface of the zebra hide. Outlines of the shell area of horse and mule hides are given.

Much of the success in utilizing horse hides lies in the ingenious method of trimming them. In cutting off the butt the star like patterns of the hair in the flanks are used as guides. In this way better fronts are obtained than in Europe where the butts are cut 30 to 40 centimeters longer and at the same time the entire shell is within the butt even for mules. The average length of the butts is 50 to 55 centimeters with a minimum of 40 centimeters and a maximum of 80. A sketch is given for trimming a hide into fronts, butt, strips and hind shanks. The fronts, butts and shanks are tanned separately, the latter being pickled and sold thus, to be tanned for work gloves.

The structure of the butts indicates their fore tanning treatment. The salted ones are soaked 1 to 2 days, the dry ones 6 to 14 days with drumming about 3 times and passing through fleshing machine with dull knives. They are limed from 6 to 14 days and since the grain has no value the percentage of sodium sulphide can be high, 3 to 5 per cent on weight of the hides. Relatively old limes are used. As the butts are very irregular fleshing must be done by hand and with care to remove all of the white layer up to the red flesh. The hind shank pieces are cut off, fleshed by machine and pickled. Attempts to make imitation goat with these pieces have not been successful because of the prolonged liming of the butts and the pieces cannot be trimmed off before liming, as it is not possible to determine then the extent of the shell layer. The butts are bated with 1.5 per cent Oropon for 3 hours at 35° C., then tanned generally with a mixture of 70 per cent quebracho and 30 per cent gambier. After tanning, the butts are treated in dilute sulphuric acid and finally in a sumac bath. They are oiled by hand with a mixture of 80 per cent degras, 15 per cent fish oil, and 5 per cent tallow. The butt is shaved, split into a shell layer or "spiegel" of uniform thickness which is brush dyed and finished.

For imitation goat, the fronts are tanned by the two bath chrome process. Soaking and liming must be carefully and quickly done to prevent loss of hide substance. To help the grain, calcium chloride to the extent of one-fourth of the sodium sulphide is added to the limes. Bating is done with 0.5 per cent Oropon on the white weight for 1½ hours at 35° C. In pickling 184 kgs. of salt and about 7½ liters of sulphuric acid are used per 100 fronts, adding after an hour about 92 kgs. of salt and 3¾ liters of acid. The skins are left then for 24 hours in a drum, turning latter occasionally, then pressed, turned in an open drum to further dry, shaved, and weighed. They are then paddled in 113½ liters of old pickle liquor per 100 fronts, and about 151½ liters of water and 1.8 to 2.3 kgs. of sodium bichromate per 46 kgs. of shaved hide are added. After 1½ hours they are given the second bath of 5½ to 7 kgs. of thiosulphate with 920 grams of sulphuric acid for each 4.6 kgs. of

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thiosulphate. After 3 hours, neutralization is done in a 2 per cent borax solution at 45° C. Coloring is done in paddles with 1.5 per cent of nigrosine and 1 per cent of logwood. A light dressing with a mixture of 80 per cent sulphonated fish oil and 20 per cent soap is given, the leather is then set out, dried, mulled, staked, dried in frames and restaked. A finish of albumin, nigrosine, Iceland moss and ammonia is given in three applications, glazing after each one.

For patent or enamel leather the fore-tanning processes are practically the same as above, care being taken to fix the grain as much as possible. Pickling is done in a 1 per cent acid and 10 per cent salt solution in drums for 6 hours and the tannage is made with Tanolin or a liquor of 10 parts of bichromate, 10 parts of acid and 5 parts of glucose, using 4 per cent of bichromate on white weight and adding 4 per cent of salt to soften the grain. Tanning is done in drums in 4 hours, then neutralized with 0.5–1.5 per cent of sodium bicarbonate. After drying, splitting and buffing the butts are completely neutralized with 1 per cent of bicarbonate, blacked, lightly oiled and dried in frames. The leather is then degreased, which should always be done when destined for export or long storage. The varnish or finish works better on the lightly oiled leather but does not adhere firmly. Three applications of linseed oil and pyroxyline mixtures are made.

The hind shank pieces are tanned by the two bath process using 30 per cent of thiosulphate and high acid content in the second bath to obtain a complete precipitation of sulphur and consequently extreme suppleness. The leather is dyed yellow with fustic and made into work gloves.

The strips cut off the front edge of the tanned butts beyond the shell are set out, dried, buffed, dyed and worked up into small leather articles.

R. W. F.

Adsorption Phenomena. By E. Stiasny. *Coll.*, **619**, 453-8 (192). Adsorption is a surface phenomenon but is often not easily distinguished from chemical action. The following facts may assist in recognizing adsorption. A temperature increase has little or a slight retarding action on adsorption while it accelerates a chemical reaction usually greatly. The order in which different substances are adsorbed may aid, for example the three chloracetic acids are taken up to the same extent by charcoal and hide powder and the action of hide powder must therefore be the same as that of carbon. Also adsorptions are reversible; however they may be so slightly reversible that the reversibility is not apparent as in the case of some dyes, or secondary changes may occur such as penetration of the adsorbed substance into the adsorbent (iodine into charcoal) or chemical changes may occur such as oxidation, polymerization, or hydrolysis. It is a question whether an attempt should be made to draw a sharp distinction between adsorption and chemical action and here theoretical views are of interest. The physical theory, that a substance is adsorbed at the surface if it lowers the surface tension of the

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solvent, was derived by Gibbs from thermodynamical considerations but the interfacial tension, liquid-solid, can not be measured experimentally. Haber considers that the residual or unbalanced valence of the surface molecules causes adsorption, and Michaelis (*Biochem. Zeit.* **94**, 240) supports this view with much experimental evidence. On the other hand Pfeiffer (*Zeit. f. angewandte Chem.* **34**, 350) holds the view that adsorption is purely chemical, and Paneth showed that at complete saturation only 17 per cent of the surface was covered. Finally there is the view that adsorption is purely electrical. Wool which moves to the anode adsorbs methylene blue and other basic dyes readily but adsorbs very little crystal violet or other acid dyes. This difference is intensified by increasing the negative charge on the wool by adding hydroxyl or phosphate ions, while if the wool is charged positively by adding hydrogen or barium ions the effect is reversed *i. e.*, acid dyes are adsorbed more than basic. There are adsorptions however which can not be explained by any of these theories.

I. D. C.

The Determination of Free Sulfuric Acid in Leather. By C. Van Der Horven. *Coll.* **619**, 458–68 (1921). No satisfactory method for the determination of sulfuric acid in leather has yet been found. The method of Jean (*Revue Chim. Anal.*, 1895 p. 3, 13) is not accurate because alcohol does not extract the acid probably because it is non-electrolyte. Kohnstein's method (*Coll.*, 1911 p. 314) based on the use of magnesium bicarbonate gives high results if chlorides are present due to the formation of magnesium chloride. Immerheiser's method (*Coll.*, 1918 p. 293) depends on an extraction of the leather with water which always gives low results. The method of Procter and Searle is fairly accurate for pure vegetable tanned leather and when sulfates only are present. The author attempted to make Paessler's method (*Coll.*, 1914 p. 126, 509, 563, 567) quantitive but dialysis through parchment or collodion was unsatisfactory since enough tannin or coloring matter came through to prevent titration. The author also suggests that in Thomas's method (This Journal **9**, 504) total sulfates be determined by extracting the leather with sodium acid phosphate solution as at present, but that neutral sulfates be determined in the ash, taking care to oxidize any reduced sulfates by the addition of iodine or bromine during solution of the ash.

I. D. C.

Tannase. By K. Freudenberg and E. Vollbrecht. *Coll.*, **619**, 468-79 (1921). The determination of the splitting or hydrolysing power of tannase preparations was first made by allowing the tannase to act on hamameli tannin or on digalloylhexose from chebulinic acid and measuring the change in optical activity. The increase in activit y was later found to be the best means of following the hydrolysis. Neither of these tannins were entirely satisfactory but the methyl ester of gallic acid is acted on in the same way, is easily obtained and is stable in water (the hydrolysis per hour is only 0.015 per cent), so a comparison was made

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of the action of tannase on this ester and Chinese tannin and digalloylglucose. The rate of splitting of the ester was found to be intermediate between that of the two tannins. The splitting power of tannase may therefore be determined by use of this ester, unless new methods for preparation of the tannase are devised in which case the comparison must again be made Titrations should be made in strong light with N/40 sodium hydroxide and using highly colored litmus paper as an outside indicator. The concentration of ester or tannin should be adjusted so that the solution to be titrated contains from one-half to one-third per cent gallic acid and a blank of 1 per cent should be subtracted from all titrations. The optimum temperature for action of the tannase on the ester was 33° C. and the most suitable concentration was ½ per cent. The splitting was not a monomolecular reaction and the amount of tannase was not strictly inversely proportional to the time required for equal splitting. Therefore the splitting power of a tannase preparation is defined as the number of milligrams necessary to half hydrolyse 1.082 grams of gallic acid methylester (= 1.000 grams of gallic acid) in 24 hours at 33°. Salts with a buffer action, as sodium acetate or gallate, interfere with or prevent titration but the salts naturally present in tannase do not influence the titration.

I. D. C.

The Investigation of Leather with Röntgen Light. By W. Moeller. *Zeitsch. für Led. und Gerb. Chem.*, **1**, 41 (1921). An investigation of hide and leather fiber with the X-ray by the method of Scherrer. The author states that this investigation showed that the individual particles of which the fibers are composed, are crystalline and their arrangement corresponds to the micellar-hypothesis of von Nägeli, that is, arranged parallel to the principal axis. Tanning with a variety of tanning materials does not change the crystalline property of the hide micells. Radiographs are shown of four kinds of leather, comparing the X-ray absorption of grain and cross section exposures with a layer of the material used for tanning. The four leathers were vegetable, chrome, iron and chamois tanned leathers and the four materials with which they are compared are solid untreated quebracho extract, chromic oxide, ferric oxide and dégras. It is shown that the permeability of leather to X-rays is a function of the permeability of the tanning material used. The grain surface exposures are homogeneous in appearance. The cross section exposures, with the exception of the chamois leather show dense layers on the grain and flesh. Just under the dense grain there is a light streak below which there is another dense streak. The middle of the cross section is light. The author considers that these dark streaks may be caused by the unequal distribution of tanning material, or by a difference of density, or by the presence of heavy spar or magnesium salts.

G. W. S.

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The Course of the Hydrolysis of Leather with Fahrion's Boiling-Test. By W. MOELLER. *Zeitsch. für Led. und Gerb., Chem.*, **1**, 47 (1921). In 1908 Fahrion published a method for testing leather which consisted of subjecting the leather to the action of hot water. [*Coll.*, 1908, 495, Abst., This JOURNAL, **4**, 60 (1909).] Fahrion considered that the truer the tannage the less material would the leather give up to water when subjected to this test. Bark tanned leather was considered as a kind of pseudo-tannage because of the relatively large amount of material given up to water under the conditions of this test, or the low water resistance, so called. Fahrion considered that true leather did not yield gelatin on boiling with water and evidently considered the organic constituents dissolved by the hot water as gelatin and that different leathers yielded different amounts of gelatin in the hot water test. The author subjected chamois, quinone, tannin, quebracho, one-bath chrome and formaldehyde leathers to Fahrion's boiling-test and investigated the results. Besides the total solids removed by the hot water, the amount of hide substance in solution was also determined. It was found that leathers with a so-called low water resistance (giving up a high amount of soluble matter), like leather tanned with tannic acid and quebracho, actually gave slightly smaller percentages of hide substance than those with a high water resistance, like chamois and quinone leather. Leathers of the latter type gave up soluble matter to the water which consisted almost entirely of hide substance or decomposition products of hide substance while the amount of hide substance given up by the former type was only a small percentage of the total amount of residue. The formaldehyde leather yielded over 50 per cent of its substance in this test which is claimed to substantiate the views of the author that aldehyde leather is not completely tanned because of insufficient time for action of the aldehydes. A leather tanned in an acid solution of chrome alum yielded its entire substance in the test which demonstrates that chrome alum without the addition of soda does not tan. The experiments contravert the assumption that different kinds of leather yield much or little gelatin or hide substance when subjected to hydrolysis with hot water. They demonstrate that all completely tanned leather, irrespective of the kind of tanning material, yield relatively little hide substance. The author considers that this test can be used to determine the extent to which a leather is tanned. If the amount of hide substance in the filtrate exceeds 9–10 per cent of that existing in the leather then the leather can be considered incompletely tanned.

G. W. S.

PATENTS

Tanning. British Patent 168,937. J. I. BAMBER AND C. M. OWEN, both in Warrington. May 1, 1920, No. 12067. Relates to apparatus in which a number of hides or skins immersed in tanning pits are suspended from a carrier frame reciprocated by crank mechanism and pro-

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vided with rollers by which it runs on runways having the form of a sector of a circle, and consists in reciprocating the carrier through crank or eccentric motion, by means of an angularly disposed cord or chain.

Preserving Hides, Etc. British Patent 169,468. H. C. Ross, H. C. Marris and Walker & Sons, Ltd., Bolton. March 26, 1920, No. 8860. A composition for preserving hides and skins, also applicable to sausage skins, fish livers, etc., contains the end products of the action of enzymes which produce undesirable changes, such as peptones, amino-acids and ammonia. Inhibitors of enzyme action, such as common salt, calcium chloride, and potassium oxalate, and germicides such as carbolic acid and xylene may also be added. The material may be applied as a powder, but is preferably made into a paste with glycerine or like hygroscopic material.

Treating Hides and Skins. British Patent 169,730. H. C. Ross and Walker & Sons, Ltd., Bolton. March 25, 1920, No. 8739. Comprises a process for depilating hides and skins in which extrinsic bacteriological or saprophytic enzymes are inactivated whilst the action of thrombase (thrombin) which is stated to be found in the skins, especially at the roots of the hairs, is encouraged or activated. The extrinsic enzyme system, to which the term "saproprotease" is applied, is inactivated by the use of end products of proteoclastic enzyme action such as ammonia or compounds producing ammonia, amino acids, skatol, and indol. The intrinsic enzyme, thrombase, is activated by the addition of easily dissociated calcium salts or compounds such as the lactate or polysulphides thereof. The activator and inactivator are mixed together in the form of a solution, the inactivator preferably comprising a one per cent solution of ammonium hydrate. The action of the intrinsic enzyme may be assisted by the addition of trypsin or other proteolytic enzymes which will work in an alkaline medium. The depilation is stated to be effected without destroying the epidermis, so that comparatively large sections thereof with the hair attached can be removed. Subsequent bating is unnecessary. In preparing dressing leathers, the solutions are heated, whilst for sole leathers cold liquids are employed, these allowing imbibition or plumping to take place to a greater extent. The process may be employed in the treatment of diseases but no claim is made for this application of the invention.

Synthetic Tanning-Agents. British Patent 169,943. J. Y. Johnson, London, July 3, 1920, No. 22478/21. A tanning preparation which gives a light-coloured leather is prepared by adding a decolorizing-agent, such as chlorine, hypochlorites, oxalic acid, or formaldehyde, to the crude sulphonation product of crude anthracene, crude carbazole, anthracene waste, and the like.

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VOL. XVII APRIL, 1922 NO. 4

THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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BUREAU OF EMPLOYMENT

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Notice of positions vacant and situations wanted will be kept on file at the Secretary's office.

Prompt co-operation of the chemists in the trade will result in a mutual benefit to those seeking employment and those desiring chemists.

POSITION VACANT

LEATHER CHEMIST (male or female) with a little experience in the making of analysis and color tests. Position vacant in Chicago. For information communicate with the Secretary.

THE NINETEENTH ANNUAL MEETING
June 21st, 22nd, 23rd

The result of the post-card ballot has shown so overwhelming a sentiment in favor of Bigwin Inn that the Secretary now can announce definitely that the next Annual Meeting of the American Leather Chemists Association will be held at Bigwin Inn, Lake of Bays District, Canada, June 21st, 22nd, and 23rd. Full details will be supplied later, but reserve these days for the meeting now.

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The promises of attendance and the hearty support accorded the idea of going to Bigwin Inn for our meeting give every assurance of a meeting that will be exceptional in point of numbers and enthusiasm.

The program committee already is at work and in touch with several men, eminent in their field, who may be expected to present papers at our Convention, which will make the meeting noteworthy.

In order, however, to make the meeting the real success which we all desire, all members must work together to effect this result. Not only is the presence of each one needed, but his co-operation as well through the presentation of papers embodying a record of his studies and experiences.

The Secretary will be glad to hear as early as possible from those who have papers to present.

REPORT OF COMMITTEE ON HIDE POWDER

The Committee on Hide Powder has tested the batch of hide powder which the manufacturer proposes to supply when the stock of Official Hide Powder No. 1 is exhausted.

The Committee finds this hide powder as nearly like No. 1 in physical and chemical properties and in working qualities as can reasonably be expected.

A series of non-tannin determinations made by the members of the Committee on a wide range of tanning extracts, liquors, etc., using their stock No. 1 hide powder and the sample, gave a grand average non-tannin figure for hide powder No. 1 of 14.06, and for the sample of 14.05.

The Committee therefore unanimously approves the batch from which the sample was submitted as Official Hide Powder No. 2 and the manufacturer is hereby authorized to distribute this batch of hide powder under the name of Official Hide Powder No. 2.

Should any members of the Association find any grave discrepancies between lots of Official Powder supplied by the manufacturer, report should be made promptly to the Chairman, giving all the particulars and accompanying with samples.

For the Committee,

March 1st, 1922. F. H. SMALL, *Chairman.*

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PROPOSED PROVISIONAL METHOD FOR SAMPLING LEATHER

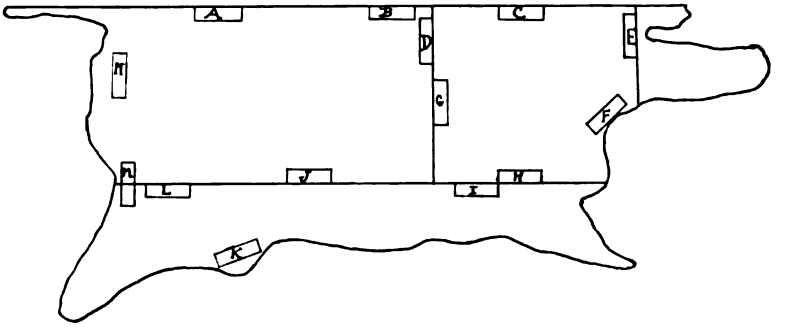
The following method for the Sampling of Leather has been submitted to the Secretary as a provisional method by the Committee for Sampling Leather:

The Committee of the American Leather Chemists Association which has investigated the Sampling of Leather proposes, as an addition to the present methods of the Association, the following as a method for the sampling of leather.

This proposal is made by the Committee unanimously, save that Mr. Orthmann dissents as follows: "I do not believe that the method as outlined by the Committee is applicable to the sampling of light chrome tanned upper leather, and that further work should be done in regard to sampling lighter leather for analysis before the same be recommended to the Association for adoption."

Provisional Method for Sampling Leather

To sample any one of the ordinary commercial cuttings of leather, samples must be cut from each piece sampled of the size and in the locations designated below.



	Single	Double
Belly	I-L-K	——
Shoulder	C-H	G-H
Bend	A-B-J	N-D-J
Butt	A-C-J	N-E-J
Side	A-C-K	N-F-M

It is much more difficult to sample satisfactorily double than single bends, butts and hides and wherever possible, the sampling prescribed for single bends, butts and hides should be followed.

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The location of the samples is shown only relatively, because of the wide variation in the size of hides, skins, etc., but the relative location shown in the diagram must be adhered to strictly.

Each sample is to be cut of rectangular shape, approximately 2½ inches x 8 inches, ½ inch then being removed from the uncut edge so as to leave the final sample for analysis exactly 2 inches x 8 inches. The whole of each sample is to be prepared for analysis by sawing, planing or other approved method and the leather so prepared from each sample must then be mixed with most scrupulous care to insure a uniform mixture. Equal weights are now taken from each of the prepared samples obtained from the piece sampled, and these, when thoroughly mixed together, constitute the sample for analysis.

When samples are taken from more than one piece in any one lot, all the samples from the same location are to be prepared as above—thoroughly mixed and then equal weights taken from each of the mixtures so obtained to constitute the sample for analysis.

Sawed leather is exceedingly difficult to mix and unless exceptional pains are taken with the mixing to insure a uniform mixture, a representative sample will not result.

F. H. SMALL,
Chairman

For the Committee.

FERMENTATION IN TANNERY LIQUORS

(*A Suggestion*)

By B. S. Levine

Received February 10, 1922

The unused undiluted bark extract, if it contains tannic acid to about 15 per cent, is antiseptic for nearly all microorganisms and is a disinfectant for most of the bacteria and yeasts. It is a disinfectant for the molds as well, with the exception of *Aspergillus Niger, Penicillium Glaucum,* and *Aspergillus Oryzoe,* which will thrive luxuriantly on high percentages of tannic acid, breaking it down to its building parts and also causing the formation of secondary decomposition products. It is evident then, that if for any reason a tanner wishes to keep his original bark extract in an unfermented state for some time, that he has to

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look for means of preventing the growth of molds; and as the latter grow only on the surface of the extracts, the problem resolves itself in keeping the surface of the extract in an uncontaminated condition. From the fact that sealed containers filled with the bark extract frequently blow up, it must not necessarily be inferred that anaerobic bacteria were responsible for that. Though such may at times be the case, the nearest probability is that the mycelia of the species of molds above referred to have extensively penetrated throughout the extract and have produced so much of the enzymes (ferments) that the effect was brought about. To avoid this, again, prevention of the growth of molds rather than that of the bacteria and yeasts, should be aimed at. This can be accomplished either by sprinkling over the surface of the extract of some thymol, certain copper salts, or of covering the surface with a thin layer of petroleum oil. In all these cases the prevention of the growth of the molds on the surface of the extract will be lasting, but it can be easily seen that some objections may be raised against the use of the above mentioned reagents, in which cases resort may be had to a thin copper sheet which could be put over the extract so as to come in contact with the entire surface of the extract. I assume that the solving action of the extract on the metallic copper will for all practical purposes be entirely negligible, yet the germicidal effect be highly efficient. It will also be inexpensive as the same copper sheet may be used indefinitely.

Regarding the diluted extract, or those extracts which are poor in the percentages of tannic acid, the problem is somewhat a different one. In the latter extract the bacteria and the yeasts, as well as the molds, will grow rapidly and will bring about deterioration of the extract. It has been shown by some investigators that yeasts and bacteria ferment at first the carbohydrates and the glucosides contained in the bark extracts, producing various acids which are beneficial to the proper tanning processes. It is, therefore, desirable that at the time of immersing the hides in the extract, a certain state of fermentation be reached, and the growth of bacteria and yeasts, therefore, be encouraged. If, however, for some reason the use of the liquor has to be postponed for a time it is not only desirable, but necessary to delay such fermentation for a time for the following reasons:

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In a medium favorable for the growth of bacteria the latter appear in cycles. First there appear those which thrive best under conditions prevailing at the start; then, as there will have been produced enough end products in the form of acids and various toxins to arrest their own growth or even to cause autolysis, there will appear in the medium those organisms for which the conditions resulting from the growth of the former will be most favorable, and so on until all the organic substances have been transformed to simple inorganic salts. Further cycles will then take place, but in these for the present we are not interested.

In the bark extracts properly diluted for bacterial and yeast growth, the cycles have been shown to be similar to those that are taking place during the process of ordinary putrefaction, namely, there will first appear the aerobic bacteria and the yeasts which attack the carbohydrates and the glucosides. They will use up all the free and diluted oxygen of the media and cause the prevailence of anaerobic conditions favorable for those mycroorganisms which are able to live under the conditions of acidity developed by the previous cycle. Attacking the tannins and the nitrogeneous substances, especially in the case of a slightly used liquor, the microorganisms representing the second cycle produce a fairly large amount of ammonia which more than neutralizes the acids produced by the organisms of the first cycle, and prepare the proper conditions for a third cycle, organisms of which and their ferments strongly attack and rot, so to say, nitrogenous substances of all kinds, including leather. It must not be thought, however, that there is a sharp line of demarcation between these cycles with regard to the time of their appearance in the tannery liquor. Due to some differences in conditions, such as the difference in temperature or acidity at the different depths of the liquor, representatives of the first cycle may prevail in one part of the medium, whereas those of the second and third cycles will be found prevailing in other parts. Thus, it will happen that in a highly fermented vat at one time there may be found leather in different stages of disintegration. It then becomes evident that if the use of the liquors in which conditions for yeast and bacterial growth obtain, is to be delayed, it is necessary to prevent their fermentation, other-

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wise they will soon be brought to a stage at which they will not only lose all their tannins, but will also cause disintegration of the leather or at least soften it in a comparatively short time.

Fermentation, therefore, must be stopped. But how shall it be done? The use of the well known disinfectants and antiseptics such as carbolic acid, bichloride of mercury, various copper salts, formaldehyde, antiformin, chloride of lime, sulfurous and various other acids may be suggested, but when it comes to a consideration of a general application, an objection may be raised against each of the above enumerated reagents. Some of them are too expensive and almost all render insoluble certain constituents of the bark extract, or else their presence has an unfavorable effect upon the leather proper. Here again the contact of the liquor with metallic copper may bring about the solution of the problem. Such contact could be accomplished by preparing a copper sheet shaped so as to come into immediate touch with the entire contents of a container when given a certain motion.

If the liquor is mobile enough, it will keep in motion due to the changes in the temperature outside, thus doing away with the necessity of stirring it every now and then to insure temporary contact of the liquor with the metal.

It has been shown in water purification that such a procedure is highly efficient. Copper containers for water supply have been recommended and used in the army for the same purpose, and there is no reason why the same should not work in the prevention of fermentation in the tannery liquors.

The bibliography which might be recommended follows:

1 Fermentation in Tanning Liquors. *Ledertechn Rundschau*, 7, 273-4 (1915).—Hugo Kuhl.

2 Precautions to be Taken When Stoppages Occur in the Tannery. *Der Gerber*, 792, 793, 239, 253 (1907).—W. Eitner.

3 Fermentation in the Tan Yards. *Leather Trades Review*, **43**, 23.—L. A. Groth.

4 The Bacteriology of the Leather Industry (A Bibliography). *Jour. Soc. Chem. Ind.*, **30**, 266-7.—J. T. Wood.

5 Bacteriology of the Tan Liquors. *Der Gerber*, 1895-6.—Andreasch.

WAUKESHA, WISCONSIN.

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GALLOTANNIN *

By M. Nierenstein

Although the chemistry of gallotannin has attracted such workers as Scheele, Davy, Liebig, Berzelius, Schiff, and many others, the results so far obtained have been disappointing. The author has devoted nearly twenty years to the chemistry of gallotannin, but has so far failed to elucidate this problem, and the same must be said regarding the elaborate researches of Emil Fischer.

It is not intended in this paper to give a full account of the chemistry of gallotannin, but the following "milestones" of its history give a good general view of the subject. Gallotannin, or tannic acid, as it is generally referred to, was first isolated by W. Lewis in 1763; this was followed by the discovery of gallic acid in 1768 by Piepenbring. Scheele later (1787) showed that gallotannin was related to gallic acid, which was confirmed by Liebig (1843), who found that gallotannin is apparently quantitatively hydrolysed to gallic acid on boiling with dilute sulphuric acid. In 1871 Schiff obtained on heating gallic acid with arsenious acid an amorphous substance which gave all the tests for gallotannin, including the precipitation with gelatin. He assigned to this substance the constitution of digallic acid and thus claimed to have synthesised gallotannin. Since then it has frequently been assumed that gallotannin is identical with digallic acid.

Schiff's digallic acid formula for gallotannin became, however, untenable when Flawitzki discovered in 1895 that gallotannin is an optically active substance. His observation was confirmed in 1898 by Walden, who also showed that gallotannin possesses a high molecular weight (about 1,500) and has no electro-conductive properties. Schiff's digallic acid has, however, a low molecular weight, has no asymmetric carbon atom, and possesses a free carboxyl group.

Such was the position when the author commenced his work on gallotannin in 1901. His investigations on this subject may be divided for clearness sake into four main phases:—

* Reprinted from *J. S. C. I.*, 41, 29T (1922).

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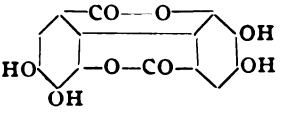
(1) The establishment of the constitution and the synthesis of ellagic acid (formula I) in 1905 (ellagic acid being a well-known oxidation product of gallo-tannin).

(2) The isolation of crystalline digallic acid (formula II) from gallotannin in 1910.

(3) The reduction of digallic acid to leuco-digallic acid (formula III) in 1912. This product contained an asymmetric carbon atom and was resolved into the two optically active forms.

(4) The identification of *d*-leucodigallic acid amongst the disintegration products of gallotannin in 1912.



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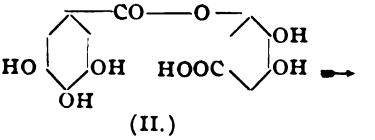

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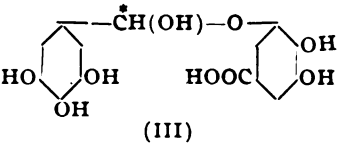
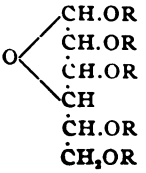


(III)

Encouraged by these results, it was suggested by the author in 1912 that gallotannin was probably the anhydride of polydigalloylleucodigallic acid. Such a formula would have accounted for the different facts known at the time. The formula was, however, withdrawn in 1914, in consequence of the discovery made by Fischer in 1912 that glucose forms an essential part of the gallotannin molecule.

In addition to showing that gallotannin is composed of gallic acid and glucose, Fischer synthesised during the years 1912 to 1918 a number galloylglucose derivatives, including pentagalloyl- and pentadigalloyl-glucose. Some of these substances resembled gallotannin to such an extent that Fischer proposed his, now well known, pentadigalloylglucose formula (formula IV) for gallotannin.



R = Digalloyl radicle.

(IV.)

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In doing so Fischer followed, however, in Schiff's footsteps in attempting the synthesis of gallotannin before its constitution had been established.

To test Fischer's formula a series of experiments were undertaken by the author which were subsequently published in 1921. They showed a number of objections to the pentadigalloylglucose formula of Fischer, the main objection being that whereas Fischer's pentagalloylglucose when methylated with diazomethane yields glucose on hydrolysis, methylogallotannin gives under identical conditions tetramethylglucose, which shows conclusively that in gallotannin four hydroxyl groups are not replaced by digalloyl radicles as assumed by Fischer.

This obviously brings us to a modified "longchain" formula of the author, *viz.*, that gallotannin is probably a glucoside of the following polydigalloylleucodigallic acid anhydride:

$$(HO)_3C_6H_2.CO.[O.C_6H_2(OH)_3.CO]_x$$
$$.O.C_6H_2(OH).CO.O.C_6H_2(OH)_2.CH(OH).O.C_6H_2(OH)_2.$$
$$O \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CO$$

or of its free acid.

The assumption of this formula is in good agreement with the following facts:

(1) It explains the high molecular weight, the optical activity and the low electrical conductivity of gallotannin.

(2) It is in accord with the observation of Stiasny (1911) that gallotannin is more acidic towards diazoacetic ester than pyrogallol.

(3) It accounts for the mutarotation of gallotannin observed by the author (1912).

(4) It explains the different phases observed by the author (1921), which occur in the formation of ellagic acid from gallotannin.

(5) It is in accordance with the formation of tetramethylglucose from methylo-gallotannin.

It must be noted that none of the last four mentioned points can be explained on the basis of Emil Fischer's formula.

In conclusion the author wishes to express his thanks to his collaborators, especially to Dr. A. Geake and Mr. C. W. Spiers.

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THE OFFICIAL METHOD OF TANNIN ANALYSIS— FURTHER OBSERVATIONS AND SUGGESTIONS

By H. C. Reed and T. Blackadder

Received March 7, 1922

In a previous communication[1] the authors advanced certain thoughts and considerations concerning the analysis of tanning materials by the official method. The basic belief was expressed that improvement in our analytical methods must be effected, by building upon the foundation already in existence, rather than by erecting a new structure upon an untested foundation. The further belief was expressed that the practical use to which these materials are to be put, should serve as a guide in seeking any improvement to the present official method.

Acting upon this belief they have made the attempt to measure the weakness of such parts of the present method as seem in the past to have drawn criticism, and, where they have believed a weakness to exist, they have further attempted to realize a method of eliminating the weakness. Some of the results of the work done have been so full of suggestion that they believe it advisable at this time to present such of these results as appear to have definite value.

Turning first to the determination of the non-tanning matter or "Non-Tannins" in the official method, a great deal of criticism has been aimed at this determination on account of the possibility of absorbing non-tanning matters. It would seem possible to reduce the amount of any such absorption by reducing the amount of hide powder used. At the same time there would be a limit to the reduction of hide powder beyond which detannization would be incomplete and matter left in the solution which would react with gelatine and which would therefore be classed as tannin. When we carry out our detannization with this minimal amount of hide powder the probability is that the time of contact would have an influence on the completeness of detannization. In other words it is to be expected that an amount of hide powder which would just fail to yield a completely detannized solution after ten minutes shaking would yield a completely detannized solution after, say, one hour shaking. The figures obtained by the authors substantiated these expectations and in general seemed to indicate

[1] H. C. Reed and T. Blackadder. This Jour., 17, 9 (1922).

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that an increase of the time of shaking up to two hours was beneficial, but beyond that time had no appreciable beneficial effect so far as detannization with small amounts of hide powder was concerned. The variation in the non-tan figure as the amount of hide powder was reduced tends to show that complete detannization can be effected with as low as four or five grams of dry hide per 200 cc. analysis solution when shaken for two hours and that the non-tan figure is not very greatly raised. A typical run of figures is shown immediately below.

PER CENT NON-TANS ON A CHESTNUT WOOD EXTRACT USING OFFICIAL PROCEDURE. QUANTITY OF HIDE POWDER AND TIME VARIED AS SHOWN.

Dry weight of hide.....	12½ gr.	12½ gr.	10 gr.	7½ gr.	5 gr.
Time of shaking.....	10 min.	60 min.	60 min.	60 min.	60 min.
Per cent non-tan found.....	13.48	13.05	13.38	13.80	15.47*

*Showed trace of tannin by gelatine salt test.

In passing it ought to be stated that in cases where the non-tan solution responded even slightly to the gelatine salt test an apparent increase of about one per cent occurred in the non-tan figure when this figure was around 15 to 20 per cent.

Remembering that in tanyard practice the fresh liquor meets partly tanned hide, and the partly exhausted liquor meets fresh hide with possibly a sharp appetite for tannin, non-tannin determinations were made adding the hide powder in two portions at intervals of one hour, but no difference was noted between this method of procedure and the method of introducing the same amount of hide in one portion.

It would also be expected that better absorption of the tans could be effected by detannizing in a more acid solution than that prevailing under official conditions. This was easily demonstrated, and it was found that by acidifying the solution slightly the absorption was increased, and that the quantity of hide powder used could be reduced in some cases to as low as three grams. As however three grams did not suffice in all cases four grams was adopted as the minimum in subsequent work.

Inasmuch as acidifying caused better absorption of tanning matter the question arises as to how much acid can or should be added. In studying this point formic acid in increasing amounts was added to the analysis solution. Hide powder in the amount

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of 4 grams dry to 200 cc. solution was added and shaken for two hours. The effect of the acid was in general found to increase with increasing addition up to approximately 0.05 per cent of acid. From this point on the effect was not appreciably increased by further addition of acid. In the figures of a typical run given immediately below, the increased absorption, as reflected by lower non-tan figures, is up to a certain point very markedly shown; beyond this point the absorption apparently remains uniform. Paradoxically the non-tan solutions of oak bark which contained the greatest amount of unabsorbed matter gave no test for tannin whereas with some materials intermediate solutions reacted for tannin. We shall refer to this point again later. For reasons mentioned below officially chromed hide was not used in these tests.

PER CENT NON-TANS FOUND WITH VARYING AMOUNTS OF ADDED FORMIC ACID, SHAKING 5 GRAMS DRY HIDE WITH 250 CC. OFFICIAL STRENGTH SOLUTION 2 HOURS

Gr. formic acid added.	Oak bark extract.	Chestnut wood extract.
0.005	22.96	——
0.065	22.43	——
0.200	——	14.73
0.025	21.70	——
0.040	20.94	14.46
0.050	20.77	——
0.060	20.54	14.28
0.080	19.99	13.92
0.100	19.90	14.16
0.120	19.64	14.12
0.140	19.53	14.27
0.160	19.58	14.18
0.180	19.61	14.18
0.200	19.61	14.18

NOTE:— The underlined figures denote that the corresponding non-tan solutions reacted to the gelatine salt test.

The use of acid in promoting the absorption thus appears capable of control, and as the higher acidity of the solution at the time of detannizing parallels tannery conditions more nearly, it seems a desirable feature in the analytical procedure.

Another question is introduced by the use of acid during the detannization and that is its effect on the lime present in the official hide powder and also upon the sulphuric acid previously absorbed during the chroming of the hide powder.

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Referring to a previous paper by one of the authors[2] figures are found showing the effect of various acids in the components of the non-tan residues during drying under conditions similar to official procedure. These figures show that the mineral acids effect a decomposition of these non-tan residues resulting in a loss in weight, whereas an organic acid such as formic is without this action. The action of the mineral acid can be noted by the appearance of the non-tan residue;[3] moreover its presence and also that of hydrochloric acid left from deliming the powder, together with lime, can be detected in non-tannin determinations made on solutions which do not contain these substances. The use of chrome alum as a pretanning agent would inevitably introduce this mineral acid effect, and experiments were therefore made to use other agents in preparing the hide powder. The most promising of these appeared to be quinone, which in neutral or just alkaline solution gave a very suitable preparation with standard hide powder. It seemed preferable however not to use quinone alone but to utilize the mutual oxidation and reduction of hydroquinone and chromic acid to quinone and chromium oxide. By means of this reaction in presence of the neutralized hide powder a combination chrome and quinone tanned powder is obtained which is very resistant to hydrolysis by water or dilute acid, and which, after deliming, gives a very low blank test under official analytical conditions. The apparance and feel of this powder are very good. The powder is of light brown color and can be rubbed to a fluffy state, after squeezing to the official water content, more readily than the officially chromed hide. The color is very uniform, there being no white specks or lumps present as is often noticeable in officially chromed hide. Its absorptive power compares very closely with that of official hide powder, despite its more complete pretannage.

The preparation of this powder removes not only the objection with regard to the sulphuric acid introduced with the chromium sulfate but also, as it is prepared in neutral solution, the hydrochloric acid is removed during the washing as sodium chloride. It can then be used according to official procedure if the solution to be detannised is acidified by the addition of the proper amount

[2] H. C. Reed. This JOUR., 2, 426 (1907).
[3] H. C. Reed. This JOUR., 17, 48 (1922).

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of a volatile organic acid such as formic. When thus used it is notable that the non-tan residues no longer give evidence of incipient charring and also that they are freely and completely soluble in distilled water, which is not the case with non-tan residues from officially chromed powder, or with residues obtained by the official method.

There is, further, the objectionable lime content of the hide powder to be dealt with. While this can probably be best handled during manufacture it was necessary for the present work to remove the lime in the laboratory. The necessity of this can be visualized by giving the figures obtained when making blank tests with water and with acid solutions of a strength comparable to analysis solutions. A distilled water blank gave a residue 0.0090 gram whereas a residue of 0.0200 gram was obtained with a 0.04 per cent formic acid solution. An analysis of these latter residues showed that they consisted largely of calcium salts. The increase in the residue due to the effect of a very weakly acid solution would probably be paralleled when analyzing tanning materials, as the acidity of the solution would be similar and the lime would be dissolved to a similar extent.

The method adopted to remove this lime from the hide powder was to take the powder after pretanning as above described and wash as rapidly as convenient with four successive portions of distilled water. This removed practically all of the organic compounds left from the pretanning and also the sodium chloride from the neutralizing. This powder was then shaken with dilute formic acid of suitable strength four times, squeezing after each treatment as in the regular washing of the officially chromed hide. Tests on the various washes indicate that the lime is removed very quickly by this procedure. A determination of the lime content of the finished hide showed 0.014 per cent lime on an absolutely dry basis. Blank non-tannin tests made with various lots of this powder ran between 0.0012 gram and 0.0014 gram per 100 cc. It would seem without doubt to be an excellent preparation of hide powder for analytical work.

By suitable choice of the volume and strength of formic acid solution used for washing the powder it is a simple matter to achieve any desired acidity in the final powder. As shown above the limits of acidity can be varied over a comparatively wide

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range without detriment to the analytical figures obtained, thus rendering the acid treatment subject to all the control required for analytical work.

When it is considered that leather chemists are now called upon to analyze materials of varying and sometimes high acid content the necessity of a lime free hide and a controllable acidity of solution during detannising is apparent. The advantage of such a hide powder as described, with respect to its freedom from lime, its low blank figure, its consistency of absorption over wide acidity range together with its very workable nature, seems to demand that it be given due consideration. The authors have studied its use at some length but feel that at present the principles involved are of more importance than the details. They therefore confine themselves to the statement that they have not noticed any untoward features in the use of this hide powder.

A further point which appears of vital moment should be included in these observations on account of its theoretical importance as well as its practical bearing. In a previous paper by one of the authors[3] attention was drawn to the important part which may be played by the non-tannin blank in analysis. Among other points attention was drawn to the influence it would have on the results of analyses of the same liquor at various dilutions It was particularly fitting that a hide powder which was known to yield a low blank should be tried out on solutions of an extract at different concentrations. The figures immediately below show the non-tan figures for several extracts, analyzed with the hide powder described, at official and twice official strength.

PER CENT NON-TANS OBTAINED AT OFFICIAL AND TWICE OFFICIAL STRENGTH. 4 GRAMS HIDE POWDER PER 200 CC. SHAKEN 2 HOURS

	Quebracho	Chestnut	Oak bark	Osage orange
Official strength	8.27	14.82	21 24	16.20
Twice official strength	6.67	13.50	19.22	14.27

The diminution in non-tans, corresponding to a rise in tans, is apparent when the concentration of the extract solutions is increased. It is notable that the difference in non-tan percentage is remarkably uniform considering the great difference in extract weights taken. This together with tests on the residues and various other tests made, convinced the authors that the question of matter extracted from the powder had no appreciable, if

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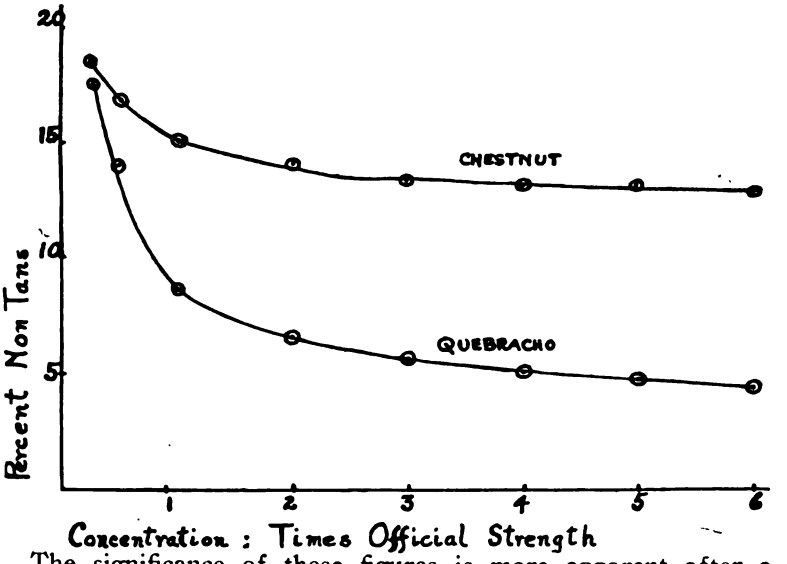
any, part in this lowering of the non-tan figure. A series of determinations was next made with more widely varying concentrations of quebracho and chestnut extracts, these being chosen as typical of the catechol and the pyrogallol tannins. The figures below were obtained.

PER CENT NON-TANS FOUND BY VARYING SOLUTION STRENGTH FROM ¼ TO 6 TIMES OFFICIAL STRENGTH. WEIGHT OF HIDE POWDER VARIED IN PROPORTION TO CONCENTRATION OF SOLUTION.

Times official strength	Quebracho	Chestnut
¼	17.69	18.43
½	14.05	16.81
1	8.69	15.14
2	6.55	14.21
3	5.61	13.37
4	5.01	13.13
5	4.76	13.26
6	4.41	12.88

The variation in the non-tan figure is progressively lower as the strength of the solution is increased. The nature of the variation is perhaps better seen in the graphical representation below.



The significance of these figures is more apparent after a consideration of the nature of the solution of a tanning material. In a previous article upon this subject[4] the authors gave their conception of the condition of tannin in solution. They conceive

[4] H. C. Reed and T. Blackadder *loc. cit.*

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of it as dissolving in three states, these states being differentiated from each other by the size of the molecular aggregates. There are first the smallest particles, existing in true solution, which may possibly be the simple molecules of the tannin. Secondly there are aggregates of colloid dimensions probably consisting of a number of the simple molecules. Thirdly there are larger aggregates which are large enough to be retained by a filter and to be classed as insolubles in our analysis. These three states will exist in certain proportions if the solution is given sufficient time to attain equilibrium.[5]

Considering now the process by which the tannin arrives at this threefold state of solution a clear understanding of solubility is necessary. Commonly when referring to matters in solution, true solution is understood, where the matter is undoubtedly in an extremely fine state of subdivision. Experience further teaches that all materials have a certain solubility in water, even materials commonly termed insoluble being to a slight degree soluble. It must therefore be granted, that the class of bodies termed "tannins" have each and everyone a certain solubility in water where it exists in true solution. In addition to this solubility they have the peculiar property of being "peptized" by water which causes a disintegration of the solid into particles of minute dimensions but not minute enough to be classed as being in true solution. These peptized particles vary in size from colloid dimension upwards and therefore give the colloid part of the solution and the coarse suspension of insolubles. Now if a minimum amount of tannin were added to a given volume of water so that the tannin was completely dissolved in true solution a radically different state of affairs exists from that which exists when a larger amount of the tannin is introduced into the same volume of water. The absence of colloidal particles would, in the highest degree of probability, preclude any tanning action

[5] It is possible that absolute equilibrium is only reached after an indefinite period and that the increase in insolubles observed on long standing of liqu rs is the result of a gradual approach to an equilibrium where a large part of the tannin would exist in the form of the large aggregates. For the purpose of our considerations the approximately stable equilibrium reached after overnight slow cooling is sufficient. That this state of equilibrium is very nearly the same as that which exists in a rapid cooled solution argues for the existence of a fairly stable state. It would appear however, that the rapid cooled solutions arriving at the same state, is a fortuitous happening and not to be depended on too absolutely.

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by this tannin.[6] As more tannin was added, the peptizing action would come into play forming colloid particles and a solution would be obtained which could tan. Furthermore the amount in true solution should be independent of the total amount of tannin added.

This consideration of the solution of tannin in the theoretical aspect would lead one to expect the type of curve obtained above, on analyzing tannin solutions at different concentrations.

Turning to the application of these considerations it seems, that when working with a concentration of "4 grams per liter" the official method errs from the best concentration for obtaining accurate results. It would be safer to work on the more horizontal portion of the curve both for reason of better concordance and ultimate accuracy. Better concordance, because a variation from the stipulated concentration will be less likely to change the proportion of inactive tannin present and ultimate accuracy, because a minimum of inactive tannin should be aimed at.

"Four grams tannin per liter" would further have to include the tannin which exists in the largest agglomerates or "insolubles" for otherwise the amount of hide which is sufficient for a low insoluble extract would not suffice for a high insoluble extract, or vice versa the amount of hide which would suffice for a high insoluble extract would be more than sufficient for a low insoluble extract and open up possibilities of non-tan absorption.

CONTRIBUTION NO. 7 FROM THE REED LABORATORIES.

A CRITICAL STUDY OF THE DETERMINATION OF THE ACTIVE CONSTITUENTS OF SYNTHETIC TANNING MATERIALS BY THE HIDE POWDER METHOD

By S. Kohn, J. Breedis and E. Crede

Received March 10, 1922.

The present paper embodies some results of our efforts to adapt the hide powder method of analysis to the synthetic tans so that it may give, as nearly as is inherently possible, a measure of their value in the same manner as does the official method for the vegetable tannins. We believe that some of the suggestions

[6] It is important to remember that the true solubility of each tannin would be different and that tests, for that concentration of the tannin solution which will not tan, when made with tannic acid would not yield us information as to the true solubility of the natural tannins. The concentration in this latter case is probably very much higher on account of the presence of at least several tannins in any vegetable extract.

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made here might be applied with advantage to the hide powder analysis of vegetable tannins also, but for the sake of simplicity we confine ourselves to the synthetic tanning materials alone.

When the hide powder method in its present official form is applied to the synthetic tans, that proportion of the material which is taken up by the hide powder is designated by the one general term "Tannin." Our work early convinced us that it is absolutely necessary to classify according to their character and function the various types of bodies which would thus fall under this general category. In effect what have so far been designated simply as tannins appear to fall into two main classes which we propose to label

1—Combination Tans

2—Adsorption Tans

although the term "tan" is in some cases a misnomer.

The basis of this classification is the conclusion arrived at as a result of careful quantitative experiments with certain typical synthetic tanning materials that their content of "Tannin" by the official hide powder method comprises two general types of bodies:

1. Those which are capable of forming a stable and insoluble compound with hide substance, and follow the characteristics of chemical reactions. This group is distinguished from the second group chiefly by the decidedly higher degree of independence from the concentration in which it is brought into reaction with hide substance and by the higher resistance to washing.
2. Those which are characterized by an outspoken adherence to the physical laws of adsorption, the main distinguishing feature of which is the direct dependence upon the concentration and the corresponding gradual removal by washing.

For a better illustration of the different influence of combination tans and adsorption tans upon the adsorption measurements for tannin determinations, we shall cite Freundlich's adsorption formula and shall call:

M. The amount of hide powder used.

X. The total amount of combination tans in the sample which is completely taken up by M.

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S. The sum of X plus the unknown fraction of the adsorption tans which are adsorbed by M.

Y. The total amount of adsorption tans in the sample.

V. The volume to which the sample has been made up.

In accordance with the laws of adsorption, we have then the following relation:

$$\left(\frac{S-X}{M}\right)^r = K\ \frac{Y-(S-X)}{V}$$

This equation means that the amount of adsorption tans taken up by the unit of the adsorbent is a function of the concentration. K and r are constants, characteristic of each tanning material.

The official hide powder method could only give strictly comparable results if the sum X + Y would follow the laws of adsorption while in reality Y is dependent and X practically independent of these laws. Or else we must assume that the proportion between X and Y is the same in all tanning materials which of course is not borne out by facts. In other words while the above formula is the correct one, the official hide powder method assumes the incorrect equation:

$$\left(\frac{S}{M}\right)^r = K\ \frac{Y-(S-X)}{V}$$

The difficulties encountered, if the official hide powder method is applied to synthetic tans, has been already mentioned in recent articles to be rather startling. For instance, it was found that the results obtained under otherwise comparable conditions vary with the degree of acidity irregularly, that is, not in lineal proportions so that no simple relation could be established between acidity and the percentage of "tannins" reported by the official method. Further the same variation in the acidity shows different variations of the percentage of tannins on different samples. Finally the entirely neutral product shows a high percentage of tannins by the official method, in spite of having no tanning effect on the hide. These difficulties were further aggravated by the fact that we had no simple and reliable method to distinguish whether the measured acidity of a sample was free sulphuric acid or sulphonic acid. All these confusing observations of the seemingly irregular influences of the degree of acidity upon the tanning de-

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termination and tanning action of synthetic tans were correlated and explained as soon as it was realized that we must distinguish between two groups of tannins, combination tans and adsorption tans, as outlined in the above. Through the full recognition of these two classes of tannins we soon were able to establish the following four points which are of great importance for our understanding of the working manners of synthetic tans.

1. The free sulphonic acids of a synthetic tan of correct acidity are combination tans.
2. The sodium salts of these sulphonic acids are adsorption tans.
3. The sodium salts of these sulphonic acids can be converted into combination tans by the addition of proper amounts of mineral or organic acids without any of the added acid remaining in free state.
4. Free sulphuric acid acts, under the conditions of the analysis by the hide powder method like an adsorption tan while free sulphonic acids are (as stated under point 1) combination tans.

It is apparent from the mere enumeration of these four main points of our observations that the results obtained by the hide powder method only require proper interpretation to be at least a satisfactory measure up to a certain point of the relative values of synthetic tans.

The Free Acidity in Syntans.

One of the first questions to be answered regarding synthetic tans is that of the proper acidity. The active ingredient of these materials being a sulphonic acid, the tanner wants to be able to satisfy himself that no other strong acids, which are not combination tans, be present.

Usually this question was attacked in that way that a method for the distinction between and for the determination of sulphuric and sulphonic acids was sought. Quite a number of methods have been suggested, most of them rather involved and none free from objections. We ourselves have spent some time studying these strictly chemical methods until we arrived at the conclusion that the problem must be attacked from an entirely different angle. While it is no doubt of high scientific interest to be able to distinguish between sulphonic and sul-

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phuric acids, the practical tanner will be more interested to know that no other acid whatsoever be present in appreciable quantities in the synthetic tan, except those sulphonic acids which are capable of combining with the hide substance to a stable compound, in other words,except those sulphonic acids which are "combination tans." While bodies taken up by adsorption are useful and desirable, the tanner will only welcome adsorption tans which are not free acids. Sulphuric acid acts like an adsorption tan but its presence is rightly dreaded. Other free acids also act like adsorption tans and while of course, in some instances, of no such outspoken obnoxious influence as free sulphuric acid, the tanner will justly feel that he prefers a synthetic tan with no other free acid whatsoever except the sulphonic acids which are combination tans.

A solution of synthetic tan will as a rule contain Na, H, Ca, etc., ions on one side and SO_4, RSO_3, Cl, etc., ions on the other side. Assuming we were in a position to exactly determine by chemical or physical measurements how these ions are paired off, such determinations would not hold good any more even after a change in concentration or temperature, much less of course after we introduce hide substance which will react with some of these ions in preference to others. We are here not interested in theories of ionization but in the functional properties of the mixture representing our synthetic tan. All we want to know is that after the hide substance has reacted upon our solution, no free acid is left in solution, or is held adsorbed by the hide substance.

From this, one can readily see that no chemical method can satisfactorily answer the question of acidity in the synthetic tans. We must resort again to the imitation of the actual tanning practice, to the hide powder method. To see whether or not a synthetic tan has the proper amount of acidity we subdivide our sample into several parts and vary the acidity above and below its original acidity by adding a known amount of alkali or acid as the case may be. We treat then each of these parts of various acidities under certain definite conditions as to concentration and time of shaking with a certain amount of hide powder. We find that starting with the sample of lowest acidity, the filtrate containing the matter *not* taken up by the hide pow-

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der will first show no acidity to methylorange in spite of the gradual increase of the acidity of the solution of the tan with which the hide powder has been shaken. As soon as more acid is added to the tan solution than corresponds to its content of combination tans, this excess of free acid, whether it be sulphuric or any other acid will, under the conditions of the experiment, not be completely removed by the hide powder, but will distribute itself between the hide substance and the water according to the laws of adsorption, and the filtrate containing the matter not taken up by the hide powder will show, from that point on, a steady increase in acidity.

It goes without saying that in order to obtain useful data the amount of hide powder, the concentration and the time of shaking have to be gauged judicially.

If a synthetic tan does not contain any excess of acid over the acidity of its combination tans the analysis by the hide powder method can be carried out along the same lines as the analysis of vegetable tanning materials.

It is important, however, to note that some tanning materials contain bodies which are capable of combining chemically with hide substance but yield compounds that are not as stable and insoluble as those of other combination tans, and which will therefore show a lower degree of independence from the concentration of the solution and a lower resistance to washing. To be exact, the definition of a "Combination Tan" should contain a definite statement, in figures, about the stability and insolubility of the compound with collagen. Before we have agreed upon strictly defined limits, we must be satisfied with making comparative observations under comparable conditions.

Before going into the details of our report, we wish to point out that the hide powder method of analysis on synthetic tans can only have as its aim to supplement tanning experiments but never to replace them. We know groups of bodies (certain uncondensed sulphonic acids, like napthalene sulphonic acid for instance) which although not being tans will in every way respond to the treatment of the hide powder method exactly like a tan, because the true character of their combination with hide substance cannot manifest itself in that time and those con-

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centrations to which an analytical method is necessarily limited. Determinations of percentages of matter adsorbed by and combined with hide powder on samples which have not previously been tested by tanning experiments extending over several weeks, are lost time and lost energy, because the figures obtained do not mean anything.

Analytical observations can and in many instances will discover which ones of a number of synthetic tan samples are superior to others but the real proof is the application under the conditions in the tannery. All we can expect from the hide powder methods of analysis is a confirmation of the tanning experiments as to the quality of the syntan and quantitative determinations of percentages which latter, however, are comparable only on samples of the same chemical nature.

We wish to emphasize here some of the important limitations which must be borne in mind in attempting to interpret the results of these analyses.

The differences between synthetic tannins of various types are of a totally different order from the differences between the vegetable tans. They possess molecular weights of an altogether different order from those of the vegetable tans and they combine with hide substance to form products which exhibit much wider qualitative differences, *e. g.*, as to permanency, tensile strength, etc., than do the "leathers" formed by the different vegetable tans. For these reasons, it is altogether misleading to compare a tannin unit of one type of synthetic tan with a unit of another, or with a unit of a vegetable tan in the same way as tannin units of different vegetable tans can be compared.

Further in interpreting these analyses there is a temptation, arising from long use of this method on vegetable tans, to lay undue stress on the tanning value of these products as tanning materials *per se*. Undoubtedly the tanning value of many of these products, apart from any qualitative differences they may bring about, lies as much in the increased efficiency they give to the use of vegetable tannins with which they are mixed, as in their value as tannins *per se*. The hide powder method in its present form throws no light whatever on the relative merits

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of synthetic tans in what is one of their most important functions, *viz.*, to increase the efficiency and availability of the natural tannins.

We have chosen four samples for our investigations, and in reporting our procedure and experimental results we have given these in greatest detail with reference to sample B for the reason that its simple composition and definite characteristics make it particularly adapted to illustrate our method.

Experimental Part.

Syntan Sample B.

Soluble Solids, Organic Matter and Correct Acidity. It is necessary to establish roughly the composition of the sample before the working details for the determination of the correct acidity (concentration, proportions, time of shaking, etc.) can be calculated. To this end the soluble solids and the amount of inorganic matter is determined and the percentage of organic matter calculated by difference. In the determination of soluble solids we found it advisable to evaporate only after neutralizing the sample completely with a measured amount of NaOH and correct the weight of the solids for the sodium introduced. Otherwise it is impossible to get a reliable figure owing to the presence of volatile acids or the hygroscopic character of the free non-volatile acids which may also affect the organic matter after a high degree of concentration has been reached.

For the determination of the inorganic matter (ash) it is best to ignite the sample as is, without previous neutralization. (Treat the ash with a little sulphuric acid and ignite again before weighing, so as to change all sodium salts to Na_2SO_4). The calculation of the organic matter from the ignition loss will then be only approximately correct. If an excess of acidity over the acidity of the sulphonic acids was present, the ignition loss will include the excess inorganic acid. If on the other hand, the sample was underacidified, the sodium of the sodium sulphonates will be reported not as Na_2 but as Na_2SO_4, leading to too high a figure for ash and too low a figure for the organic matter. Only if the composition of the syntan is fully known so that the equivalent weight of the sulphonated compounds can be calculated is an exact determination of the organic matter

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possible by igniting a strictly neutral sample and correcting the observed ignition loss by multiplying it with the factor $1+\frac{48}{W-48}$ "W" stands for the equivalent weight of the sulphonic acid and $48=\frac{SO_4}{2}$. As stated above, however, an approximate determination of the organic matter by igniting the sample as is, will suffice for the purpose on hand, namely to indicate how strong a solution of the syntan shall be used with a certain amount of hide powder so as to give comparable figures in the determination of the "correct acidity."

As the "correct acidity" is the acidity at which a solution of synthetic tan, after being shaken with hide powder, shows neither free acid nor tan in the filtrate, it is of course important to find out how high a percentage of the total amount of tan can yet be detected in the filtrate by the gelatin salt reagent. We found that one gram of sample B dissolved in one liter of water, which would mean about a 0.012 per cent solution of organic matter still gave a decided test for tannin with the gelatin salt reagent. Consequently if we would be satisfied with an approximation of 97 to 98 per cent of the actual tannin content, we would be within this limit if we dissolve 40 grams of sample B in 1,000 cc. of water and shake it with so much hide powder as will exhaust this solution in a reasonably short time, say 10 minutes. Too high concentrations and excess of hide powder must be avoided to reduce the error due to adsorption of free acidity to a minimum. In carrying out the determination of the correct acidity, it is preferable to start the observation from a point of deficiency of acid, so that the filtrate will be neutral but show a content of tannin upon acidification and repeat the shaking with hide powder on gradually higher acidified samples until the filtrate shows no or only a very faint test for acidity against methyl-orange and also no or only a very faint test for tannins with the gelatin salt reagent even after acidification. If the observations are started on overacidified samples and the attempt is made to reach the point of correct acidity by gradual neutralization, one will get in many instances the same figure, although under certain conditions the results may be thrown off by disturbing influences, such as retarding of the tannage by too much acid and

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removal of a good deal of excess of acidity by adsorption. The adsorption of the sodium salts of the combination tans on the other hand will never be so great that not sufficient quantities would remain in the filtrate to indicate a deficiency of acid with the gelatin salt reagent.

Forty grams of sample B were dissolved to one liter of water. One hundred cc. of this solution were neutralized with 20 cc. N/10 NaOH and evaporated to dryness. This gave a percentage of soluble solids of 27.7 per cent after the correction for the sodium introduced The ash content was determined to 15.2 per cent which gave a figure for the organic matter of 12.5 per cent.

For the determination of the correct acidity 100 cc. samples of the above solution containing approximately 0.5 gram of organic matter were treated with 5 grams air dry hide powder, starting with low acidity and gradually increasing same in the consecutive samples until the filtrate was both neutral and detannized.

The correct acidity of the above samples was determined to be 5.0°. One degree of acidity shall signify that 1 cc. of N/10 NaOH is required for the neutralization of 1 gram of the syntan.

Determination of Percentage of Combination Tans.

We shall first report in Table I, figures obtained on sample B of different degrees of acidity with the official method. We do this to demonstrate how useless an analysis by this method is if a synthetic tan is not made up to the correct acidity or if it contains both combination tans and adsorption tans.

TABLE I.

Degree of acid.	Results by official method. % "tannins"	Actual contents calculated		
		Comb. T.	Ads. T.	Total
0.0	4.8	0.0	11.0	11.0
1.0	5.3	2.0	8.8	10.8
3.0	7.6	5.9	4.4	10.3
5.0 (correct acidity)	9.9	9.9	0.0	9.9
15.0	12.5	9.9	5.0	14.9

At zero acidity the 9.9 per cent sulphonic acids are converted to 11.0 per cent sodium sulphonates which follow the law of ad-

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sorption. Upon addition of each degree of acid about 2 per cent combination tans are formed and about 2.2 per cent adsorption tans disappear.

At the correct acidity the official method will give the correct content of combination tans in this instance because sample B at the correct acidity does not contain any or only very small quantities of adsorption tans. The absence of adsorption tans as well as the independence of the combination tans from the concentration can be demonstrated by shaking the same amount of hide powder and sample B in volumes varying from 100 to 350 cc. whereupon the figures obtained for "tannin" will vary only little from the figure obtained under the conditions of the official method.

That the sodium salts of the combination tans of B follow the law of adsorption is shown in Table II which contains the results obtained on the perfectly neutralized sample. For each determination 200 cc. of a solution containing 80.0 g. of B per liter were used.

TABLE II.

SEE FREUNDLICH'S ADSORPTION FORMULA CITED ABOVE.

Amount of hide powder used (wet)	Per cent adsorbed	Per cent not adsorbed
12.5 gr.	1.8	9.2
25.0 "	2.8	8.2
50.0 "	4.1	6.9
75.0 "	5.0	6.0

To prove conclusively the absence of adsorption tans in sample B of correct acidity we studied the possibility of a determination of the combination tans by washing the tanned hide powder along the lines of the recent suggestions of Wilson and Kern. We found, however, that unchromed hide powder even shaken with plain water for 10 minutes will show hide substance in solution. Water acidified with organic or inorganic acids will show a considerably increasing dissolving action on hide powder. We can therefore hardly be surprised to find hide substance in solution when treating hide powder with syntans in such proportion that a great percentage of the hide substance remains untanned. The use of chromed or otherwise pre-tanned hide powder in analysis is therefore imperative.

After shaking for 10 minutes we filter and collect the filtrate and wash waters, make up to a certain volume, evaporate

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an aliquot part and obtain thus a figure for the sum of inert matter plus adsorption tans. The soluble solids minus this sum gives us the percentage of combination tans. Carried out in this way the washing is finished in less than half an hour.

If 25 grams of chromed hide powder (73 per cent H_2O) were shaken for 10 minutes with 4 grams of sample B made up to 100 cc. and washed until the wash waters did not contain any more soluble matter than corresponds to the small solubility of the collagen sulphonate we obtained in the combined wash waters and filtrate 18 per cent which deducted from 27.7 per cent soluble solids lead to 9.7 per cent combination tans as against 9.9 per cent by the official method at the correct acidity.

Samples A, C, and D

Determinations of soluble solids, organic matter, correct acidity and combination tans were carried out on these samples in the same manner as described for sample B. The data obtained are reported in Table III.

TABLE III.

Syntan	A	B	C	D
Soluble solids	35.5	27.7	63.6	35.7
Ash	3.3	15.2	16.6	4.8
Organic matter	32.2	12.5	47.0	30.9
Original acidity	22.5°	5°	9.7°	14.1°
Concentrations of solutions used in grams of syntan per liter.	18 g. 36 g.	40 g. 80 g.	12 g. 24 g.	18 g. 36 g.
Minimum acidity found to be necessary to detannize 100 cc. with 6 and 12 g. respectively of air dry hide powder in 10 minutes.	8° 14°	5° 6°	10° 15°	6° 14°
Analysis by official method at original acidity.	not detannized	9.9	29.3	not detannized
Analysis by official method at minimum acidities.	not detannized	9.9 10.1	29.9 35.0	not detannized
Analysis with unchromed hide powder at minimum acidities (with correction for the nitrogen content found in non-tans).	15.4 22.2	— —	— —	12.5 21.7
Analysis by wash method at minimum acidities.	— —	9.7 10.8	29.9 35.0	— —

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DISCUSSION

To correctly interpret the data contained in Table III we must consider the following important points. The determination of the correct acidity is a method of approximation, subject to two sources of error. First, the adsorption of free acidity; second, the limit of sensitiveness of the gelatin salt reagent. The latter error declines, the former grows with increasing concentration. Since the error due to the limited sensitiveness of the gelatin salt reagent can be easily regulated it is best to sacrifice say 2–5 per cent accuracy on that account in order to be able to work in more diluted solutions in which the error due to adsorption is smaller. For the same reason, the amount of hide powder and time of shaking should be kept as low as possible.

A synthetic tan containing combination tans of one quality only, that is, tannins which will give compounds with hide substance of the same degree of stability and insolubility, such synthetic tans, represented by sample B will have but one "correct acidity." We obtain, the closer an approximation of the "correct acidity" the more we succeed to make the two errors, to which the determination is subject, compensate each other.

If however, a syntan contains combination tans of more than one quality, that is, a certain percentage of combination tans which will give compounds of similar stability and insolubility as sample B for instance, and a certain percentage of combination tans which yield compounds of essentially lower stability and insolubility, it will be self-evident that for such a preparation more than one "correct acidity" will be found. At lower concentrations the weaker combination tans will not react at all and the minimum acidity needed to detan the sample will be limited to the percentage of stronger combination tans capable of reacting in the dilution on hand. To which acidity such preparations should be made up for use in the tannery is a question to be decided in a practical way.

As we see from the Tables, the observed correct acidity of sample B changes from 5° to 6° upon doubling the concentration. 5° is however, the closer approximation because at the dilution at which 5° was obtained, the error due to the limited sensitiveness of the gelatin salt reagent is less than $^1/_{40}$ (2½ per cent) which is sufficiently accurate and does not call for further concentration

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at which the higher adsorption of free acidity by the partly tanned hide substance is responsible for the higher figure. The samples A, C and D show at the same increase of concentration (1:2) an increase of observed "correct acidity" of so decidedly higher magnitude that it cannot be explained by higher adsorption nor by the difference of grams dissolved per liter, but no doubt is due to the fact that upon doubling the concentration the inferior tans come into play. The figures for percentages as they appear in the table are data obtained under the described conditions but should not be taken as indicating anything definite except those obtained on B. For instance, A and D could not be detannized by chromed or otherwise pretanned hide powder. If shaken with unchromed hide powder detannization was possible but the figures obtained are inaccurate on account of the increase of non-tans in the filtrate which were dissolved out of the hide powder. C could be detannized with pretanned hide powder but it showed the peculiarity that the neutral sodium sulphonates once taken up, hide powder could not be easily removed by washing, while the sodium salts of the combination tans of B behaved in every respect like adsorption tans. It is a well known fact that certain sodium sulphonates of this class are taken up by hide without in any way converting it into leather, and in this respect are more analogous to the aniline dyes than to tannins.. . The resistance to washing of certain neutral salts is quite remarkable and is being investigated.

It will suffice for the present, to point out how different the properties of syntans are and that we cannot think of devising generally applicable methods for quantitative determinations before we have not agreed upon what properties the constituents of synthetic preparation must have to be considered, used and analyzed as "tanning materials."

In several recent articles on tannin analysis the statement can be found that we must be able to define a tannin before we can determine it. We have reported our observations on the four syntans to demonstrate how important it is that an agreement be reached upon a definition containing the limits expressed in figures and how we could use certain properties of the active constituents of synthetic tans to arrive conveniently at such figures.

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SUMMARY

1—To expedite further investigations the active constituents of organic tanning materials are classified into combination tans and adsorption tans. For each group we shall have to agree upon a definition containing limits expressed in figures.

2—It is suggested to use as a criterion for the distinction between the various constituents of syntans the degree of independence from the concentration, because this criterion is more convenient and more conclusive than the one used hitherto exclusively, namely, the resistance to washing, the latter being subject to disturbing influences and not easy to define.

3—The volumetric determination of the "correct acidity" at identical variations of concentrations is a quick and reliable means for comparative observations on syntans without the necessity of involved gravimetric determinations.

RESEARCH DEPARTMENT,
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ABSTRACTS

The Use of Perchloric Acid for Kjeldahl Digestions in the Determination of Nitrogen in Leather. BY J. G. PARKER AND J. T. TERRELL. *J. S. L. T. C.*, **5**, 380 (1921). The method of Mears and Hussey for nitrogen in milk and blood was investigated for use in determining nitrogen in leather. Samples prepared by sawing gave better duplicates than those prepared by means of the plane. The following method was found to give good results in comparison with the methods in common use. There seems to be no loss of nitrogen and the time is considerably shortened.

About 0.8 gram of sample was weighed out in a small metal boat and then transferred to the Kjeldahl flask, 15 cc. concentrated sulphuric acid was added and one gram of copper sulphate, and then 6 cc. of perchloric acid of specific gravity 1.12. A small funnel was then placed in the neck of the flask and the flask heated by a small flame. After a ¼ of an hour the flame was turned full on and allowed to boil until the brown color had disappeared when the solution assumed a pale greenish appearance. The solution was then boiled for a further ¾ of an hour, the flask was then allowed to cool and the digestion diluted to about 250 cc. with boiled distilled water, keeping the flask cool during dilution. Fifty per cent caustic soda solution was added, together with a piece of clean pipe clay to prevent bumping, and the ammonia was then distilled off and collected in 50 cc. of 3 per cent boric acid solution. The collected ammonia was then titrated with N/5 sulphuric acid.

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Marri Kino (Red Gum from *Eucalyptus Calophylla*). By H. Salt. *J. S. L. T. C.*, **5**, 384 (1921). Marri kino belongs to the group of kinos, which form turbid solutions in water owing to the presence of catechin. The kinos or "gums" are not formed in the ordinary metabolic processes of the tree, but by wood-boring larvæ. By boring into the sapwood at the right time of the year a vein will form and gum flow for some weeks or months subsequently. The tree can yield kino year after year, and the jarrah forests of Western Australia contain a large proportion of marri trees. The kino contains 68—70 per cent of matters absorbed by hide powder. It is very sparingly soluble, of a very unpleasant red colour, and yields a brittle "cracky" leather.

Influence of Degree of Acidity on the Tannin Content of Solutions. By F. C. Thompson, K. Seshachalain and K. H. Hassan. *J. S. L. T. C.* **5**, 389 (1921). It has previously been pointed out by Atkin and Thompson that freshly prepared analytical solutions may differ widely in acidity. The present work shows that these differences in acidity cannot be ignored. The addition of acids greatly increase the insolubles in catechol tannins, decreases the time for filtration to optical clearness, and, in general, increases the amount of non-tannin. While with pyrogallol tannins the effects are less as a rule. Mangrove and gambier are exceptions to the general behaviour of the catechol tannins. The insolubles in mangrove are greatly increased and at the same time the time for filtration is greatly increased with increasing acid content. There is also a great decrease in non-tannins. There is no change in the time of filtration for gambier with increasing acidity.

Note on the Decomposition of Sodium Peroxide Solutions by Means of Metallic Iron. By R. F. Innes. *J. S. L. T. C.*, **6**, 4 (1922). It is pointed out that sodium peroxide is entirely decomposed by boiling water in contact with iron. It has also been found that the estimation of chrome in fresh chrome liquors can be accelerated as follows:

Pipette out the required quantity of chrome liquor into a 500 cc. conical flask. Dilute to about 50 cc., heat to 70° C., add excess sodium peroxide, avoiding an undue excess, introduce a small piece of bright sheet iron (say 1 inch x ½ inch), boil one minute, cool, remove iron, acidify, add KI and titrate as usual.

Chrome Tanning VI. The Influence of Neutral Salts on the Progress of Tannage. Part I. By D. Burton and A. Glover. *J. S. L. T. C.*, **6**, (1922). The influence of neutral salts on the course of tannage is investigated by experiments involving the determination of the absorption of the acid and chromium from chrome liquors by pelt. The penetration of the chromium is found to be retarded by sodium chloride, and to a greater extent by sodium and potassium sulphates, while the acidity is increased by the former and decreased to a greater extent by equivalent quantities of the latter. Sodium chloride is found to have a greater retarding effect on tannage (as judged from the complete absence of shrinkage under the boiling test) than sulphates under the con-

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ditions obtaining in these experiments. This is concluded to be due to their influence in raising the basicity figure of the chrome salt on the fibre to a greater extent. In conformity with previous experiments it is shown that there is a fundamental difference in the tanning properties of green and violet salts.

Chrome Tanning VII. The Determination of the Basicity of Chrome Liquors by the Electric Conductivity Method. By W. R. Atkin and D. Burton. *J. S. L. T. C.*, 6, 14 (1922). The method of Thomas and Foster for the determination of the basicities of chrome liquors by titration with a standard barium hydroxide solution, and ascertaining the end-point from the point of minimum electrical conductivity is criticised. It is shown that the presence of neutral salts vitiates the accuracy of the method and as all commercial chrome liquors contain neutral salts, the method is concluded to be unsuitable for control purposes in the tannery.

Synthetic Tannins and Their Uses in Leather Manufacture. By G. E. Knowles. *J. S. L. T. C.*, 6, 19 (1922). A general article on synthetic tannins produced from coal tar intermediates with suggestions as to their use in tanning.

Spent Tanwood Waste. By A. Harvey. *J. S. L. T. C.*, 6, 24 (1922). There are a number of uses to which spent tan can be put. It has been proposed to form it into briquettes and use it for a fuel. A number of patents have been obtained for using spent bark as a roofing material in conjunction with a bituminous binder. Spent wattle bark was successfully used at first to produce a brown paper and finally it was improved so as to give a white paper. It is possible to use the tan woods and barks for the manufacture of oxalic acid. By destructive distillation spent tan will produce acetic acid, methyl alcohol and charcoal. It is possible that the latter can be worked out as a practical process.

Extraction of Oil and Proteins from Soya Beans. By S. Satow. *Technol. Rep. Tohoku Imp. Univ.*, 2, [2], 1 (1921), through *J. S. C. I.*, 41, 64A (1922). There are upwards of thirty varieties of soya beans. Analysis of sixteen varieties showed a mean content of 18.9 per cent oil and 37.8 per cent protein. The oil is extracted with benzine as the most suitable solvent. After removal of soluble carbohydrates by means of dilute acetic acid the protein is extracted in three stages—with water, with 0.2–0.4 per cent sodium sulfite solution and with 0.2 per cent sodium hydroxide solution. The protein extracted in the last stage is suitable for lacquers or coating materials.

Influence of Electrolytes on the Solution and Precipitation of Casein and Gelatin. By J. and R. F. Loeb. *J. Gen. Physiol*, 4, 187 (1921), through *J. S. C. I.*, 41, 69A (1922). Two types of colloidal solution exist. The first type is easily precipitated by small quantities of neutral salts, the second requires much larger quantities. In the first type the particles pass into solution in consequence of swelling as the result of the Donnan equilibrium, and remain in solution as a result of the osmotic

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and electrical forces which the Donnan equilibrium necessitates. The second type is of the nature of true solution, and there exist primarily only ions and molecules, though aggregates may be formed secondarily. Measurements of the rate of solution of casein chloride in varying concentrations of acids and neutral salts indicate that the process of solution is regulated by the Donnan equilibrium and that it is of the first type. The effect of small quantities of neutral salts as precipitants is to reduce the osmotic forces and also the electric charges according to the theory of the Donnan equilibrium. Casein dissolves in caustic soda solutions essentially like a crystalline substance, and the solution is of the second type. Solutions of gelatin are also of this type, though aggregates of the dissolved particles tend to form on standing. Experiments on the solubility and viscosity of gelatin solutions as influenced by neutral salts give evidence of the existence of these aggregates.

Grain vs. Flesh Side for Leather Belts. *Shoe and Lea. Rep.*, Feb. 16, 1922, p. 45. Investigations conducted by the Leather Belting Exchange at Cornell University has produced a mass of data which leaves no reasonable doubt that there are distinct advantages in power transmission to be had from running leather belts on the grain side. Running under reasonable shop tensions the flesh side will average only 50 to 60 per cent as much horsepower as the grain side. At higher tensions the flesh side will do better, averaging from 50 to 100 per cent as much power as the grain, depending on the belt, the tension and the condition of service.

The Swelling and Gelation of Gelatin. By R. H. Bogue. *J. Ind. and Eng. Chem.*, 14, 32 (1922). Experiments have been conducted upon gelatin sols and gels that have been treated with silicates of sodium in which the ratio of Na_2O to SiO_2 in the molecule varied regularly from 1:4 to 1:1. The solutions were made up so that the actual amount of Na_2O was constant in one series, while the actual amount of SiO_2 was constant in the other series. The degree of swelling, viscosity, alcohol number, and p^H value were determined in each series, both upon the normal gelatin, which was essentially calcium gelatinate of a p^H of 5.8, and upon the gelatin which had been rendered isoelectric and had a p^H value of 4.7.

The data obtained show that the swelling and the viscosity increase, in Series 1, with a decrease in the silica content, the percentage of soda being held constant. The p^H value is shown to increase constantly, however, as the ratio $Na_2O:SiO_2$ increases. This is due to an increase in the degree of hydrolysis of the silicates. The variation in the above-mentioned properties appears to be dependent upon the p^H value, rather than upon the changing silica content. This is further evidenced by the similar behavior of Series 2, in which the silica content remains constant.

The swelling and viscosity reach their maximum value at a p^H of about 8.5, and decrease slightly at higher values. The jelly con-

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sistency, however, is solid at p^H values between 4.7 and 8.0, but at 8.5 it becomes soft, and liquefies at 9.0 and above. This affords the basis of an argument which concludes that gelation is due to and dependent upon the tendency of the substance to become solvated, the volume occupied by unit weight of dispersed phase being the determining factor. When this volume is very small or very large the jelly consistency will be small, and, at intermediate values of volume per unit weight, the jelly consistency will reach its maximum.

The results upon isoelectric gelatin are similar to those obtained with normal gelatin, except that higher degrees of swelling and viscosity are attained, because of the absence of the retarding divalent calcium ion.

The alcohol number is found to rise regularly with increasing p^H, and it is suggested that this value may be utilized for rough measurements of p^H.

A Preliminary Study of the Activated Sludge Process. By J. A. WILSON, W. R. COPELAND AND H. M. HEISIG. *J. Ind. and Eng. Chem.*, **14**, 128 (1922). A report of the progress of an investigation of the activated sludge process in the sewerage testing station of the city of Milwaukee. The first experiments showed that the variation in rate of filtration with the hydrogen ion concentration is so great as to make the control of this factor essential to efficient operation. Adding sufficient sulfuric acid to the sludge to reduce its p^H value from 8 to 3 generally reduced the time necessary for filtration by 80 per cent. But it is evident that hydrogen ion control, important as it is, is not the only factor vital to efficient operation. Sludge obtained in February when the temperature of the sewage was 12° required eighteen times as long to filter as sludge obtained in August, even though each was brought to the optimum acidity before filtering. The condition of a sludge is defined by a curve obtained by plotting the time required for filtering a definite volume under practically constant reduced pressure, against the p^H value of the filtrate over a range of from 2 to 8. The February sludge is the poorest (takes the greatest time to filter) and the August sludge is the best for the first eight months of 1921. Nevertheless the optimum of filtration for any sludge is at a p^H value of about 3.2. Subsequent experiments showed that those sludges which filtered best could be made like the poorer ones by allowing to stand, and that the poorer ones could be made to equal the better by aerating sufficiently long. From experiments in aeration with controlled temperature it was found that 22° gave better results than 11° or 34°. A study of the effect of aerating with air, hydrogen and oxygen shows that hydrogen made the worst sludge while oxygen and air improved it to an equal degree. A similar set of experiments but covering the sludge with a layer of xylene show that in the presence of xylene hydrogen and oxygen make the condition of the sludge worse and air shows very little difference from these two.

G. W. S.

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Estimation of Resin Acids in Fatty Mixtures. By D. McNicoll. *J. S. C. I.*, **40**, 124T (1921). Volumetric method:—Two grams of the fatty mixture are dissolved in 20 cc. of a 4 per cent solution of naphthalene β-sulfonic acid in methyl alcohol and boiled under reflux for thirty minutes. A blank being run at the same time. The mixture is then cooled and titrated with N/2 potassium-hydroxide in methyl alcohol. Using 346 as the combining weight of resin acids, then the number of cc. of N/2 KOH solution required in excess of the blank times 0.173 equals the weight of resin acids. Gravimetric method:— The neutralized solution obtained above is transferred to a separatory and the solution is extracted with an equal volume of a mixture of ether and petroleum ether. The soap solution is drawn off including the small amount of insoluble soap that usually forms, and extracted twice again. The united ethereal extracts are washed with a little 50 per cent alcohol and the washings added to the resin soap solution which is then acidified and extracted twice with ether. The ethereal extract is evaporated and weighed.

It is claimed that this method eliminates the faults of the Twitchell method as esterification of the fatty acids is complete with the use of napthalene β-sulfonic acid. Besides this method is easier to operate.

G. W. S.

The Biologic Evolution of Wool Scouring Waters. By P. Huc. *Halle aux Cuirs*, Dec. 18, 1921, 377-9. Some interesting observations, especially on the biologic changes of wool scouring waters, have been noted in an old manuscript by A. Buisine, dated 1887. Concentrated wash waters obtained by the progressive washing of wool and containing from 10 to 20 per cent of solids are at first clear, limpid, nearly free from carbonates and of very slight alkaline reaction. On standing they become in a few days, cloudy, and viscous, and upon acidifying effervesce. This ageing produces potassium carbonate which however soon stops. The nitrogen compounds of the suint are transformed more slowly giving a continual production of ammonium carbonate until the complete disappearance of the urea. These changes are due to micro-organisms and all chemical evolution of these wash waters can be prevented by antiseptics, as is evidenced in the case of scouring waters obtained by the process of Patry and George in which the toluene used to previously degrease the wool is carried over by the wash water in sufficient quantity to prevent any subsequent fermentation and also by the preservation without change of sterilized solutions.

With the dilute wash waters carrying about 3 per cent of solids the production of potassium carbonate is much more active and continues as long as the solution contains elements capable of forming this salt. The wash water increases in alkalinity and there forms on the surface a yellowish white film which like the solution is rich in bacteria. The deposit in the fermenting wash water also contains the same kind of

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bacteria which however are motionless. The fermentation stops only when the bacterial scum has become practically an air tight covering.

These facts show why a raw wool left for some time in a moist atmosphere or washed in its own suint can, because of the formation of the potassium carbonate, be degreased without the addition of soda.

R. W. F.

Depickling. By A. Rigot. *Halle aux Cuirs*, Dec. 18, 1921, 373-6. In depickling with calcium carbonate, the active agent is calcium bicarbonate. The latter is formed by the carbon dioxide generated as soon as the calcium carbonate comes in contact with the acid surfaces of the pickled skins. Although the bicarbonate is but slightly soluble it is continuously formed and completely neutralizes the hide. The slight solubility explains the long time required. This has led to the substitution of more soluble, active materials such as borax and sodium bicarbonate. With these two, if the amount required to neutralize all the acid is added at one time the outer surface of the hide will be neutralized and these neutral surfaces will then unite with the alkaline solution leaving the hide finally with an acid interior and alkaline surfaces. This can be readily demonstrated by comparative experiments. It will be found that the hide with calcium carbonate will fall, become opaque and neutral, while with borax or sodium bicarbonate it will remain translucent and slightly swollen, the latter being due to an exchange of alkaline swelling for acid swelling. It should not be concluded that borax and sodium bicarbonate can not be used, but rather that they offer no advantage as they must be added very gradually in order that the hide will never be in a relatively strong alkaline solution.

R. W. F.

Notes on Leather Analysis. By R. Sansone. *Le Cuir*, **10**, 508-10, 537-9 (1921). Among the physical properties of leather, one which often enters into dispute is that of strength. The strength of every lot of leather should be determined before it leaves the tannery. If a tensile strength machine is not available, approximate and fairly comparable results can be obtained by supporting the test piece in a clamp and hanging on weights until it begins to break. It is suggested that a machine for testing whole skins might be devised and after determining the average break load for each kind of leather, each skin might be subjected to a load somewhat less than this. If it withstood the test it could be sold with a certain strength guarantee. Resistance to compression is measured by partly covering a square piece of the leather with a block of wood on which weights are placed for a given interval until the maximum weight which the leather will stand without appreciable depression or damage to the grain is determined. The compressed center is compared with the adjacent uncompressed edges. The weight per square meter is often important and is determined by accurately measuring and weighing the entire skin. Flexibility is determined by bending the leather, grain side out, over the arc of a circle having a diameter

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equal to six times the thickness of the leather, or over smaller diameters until the leather breaks or cracks. Permeability is determined by gain in weight on immersing in water until in two successive intervals of 1 to 10 minutes, constant weight is obtained; or by submitting to a column of water of about 50 cm. height and 5 cm. diameter, noting the time required for penetration. Microscopic examination is often of value.

Moisture is determined at 100° to 105° C.; fats by extraction with carbon bisulphide, petroleum ether or benzene, Water solubles are obtained from the 10 grams of leather after fat extraction by soaking in 200 cc. of water at ordinary temperature for 12 hours and then continuing the extraction for 2 hours up to a final volume of 1 liter. After filtering, 200 cc. of the extract are evaporated for total solubles; this residue is then ashed to give soluble mineral matter. For non-tannins 500 cc. of the filtered extract are concentrated to 125 cc. and treated with the proper quantity of hide powder. Nitrogen is determined by the Kjeldahl-Telsch method using 0.6 gram of leather and hide substance is calculated on the basis of 17.8 per cent nitrogen in cattle, horse or pig skins, 17.4 per cent in goat skins, and 17.1 per cent in sheep skins. Sugars are obtained from a water extract as for water solubles; 800 cc. of the extract are concentrated to 200 cc.; treated with 20 cc. of basic lead actetate; filtered and 100 cc. of filtrate mixed with 100 cc. of a solution of sodium sulphate of a concentration corresponding to that of the lead acetate. In the filtrate sugars are then determined with Fehling's solution. Free sulphuric acid is determined by the method of Balland and Maljean. A correction of 0.14 per cent SO_3 is made for the sulphur in the hide.

R. W. F.

Chrome Retanning of India Dressed Kip and Goatskins. ANONYMOUS. *Le Cuir*, 10, 498–501 (1921). Detanning varies according to the previous tannage. It is generally done by first drumming in warm water and then in 2 per cent borax solution with 1 to 2 per cent of bran or poplar saw dust, percentages being based on weight of skins. The saw dust seems to blot up the dissolved tannin. Leathers tanned with other than sumac, gambier and quebracho are best detanned with 2 per cent potassium bisulphite solution followed, if a very thorough detanning is desired, by borax.

Retanning is done with chromium, and while in straight chrome tannage the per cent Cr_2O_3 varies from 2 to 4, for retannage it rarely exceeds 1. Naturally only the one bath tannage can be used as in the two bath process the chromic acid oxidizes the tannin giving a dark leather. The commercial chrome liquors give satisfactory results, but instead of using 15 to 18 per cent of a 35 to 38 Bé liquor as is customary in straight chrome tanning, 6 to 8 per cent is sufficient in retanning. It is believed that a chrome liquor reduced with glycerine gives the best results. The following formula is recommended: dissolve 13 kgs. of sodium or potassium dichromate in 24 kgs. of water, add slowly 13 kgs.

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of 66° sulphuric acid and then 5 kgs. of ordinary glycerine. On cooling dilute to 35° Bé. If extremely soft leather is desired the skins are first drummed in a 6 per cent solution of hypo for three-fourths hours. To the hypo 1 per cent of formic acid is then added and after one-half hour the chrome tanning is started.

Coloring the retanned skins differs but little from the practices for straight chrome leather except that a mordant is not necessary. Oiling is however quite different because of the presence of two types of tannages. A perfect emulsion which is stable throughout the process is essential and for this reason sulphonated oils are recommended.

R. W. F.

The Time Factor in the Neutralization of Chrome Leather. By A. Rigot. *Halle aux Cuirs*, Nov. 20, 1921, 339-45. From consideration of the neutralization of chrome liquors in their preparation for tanning it might be thought that subsequent neutralization of the leather would not be necessary. Indeed an apparently well tanned chrome leather can be obtained by simply rinsing without neutralizing, and can be curried with an emulsion of egg yolk, or an oil provided no material with a soap base is used. It might be concluded from this that neutralization is necessary simply to permit the use of soaps in currying, but such is not the case. It was the use of soaps which made evident the need of neutralization.

A poorly neutralized leather, not curried with a soap base appears at first as good as one perfectly neutralized and if not submitted to certain operations in currying and finishing does not show an appreciable difference in strength until after several months. In glazing however an imperfectly neutralized leather is submitted to the destructive action of acids set free from the chromium salts by the heat generated. Naturally this action is proportional to the degree of neutralization as well as to the extent of glazing, and it is of great importance with all leathers which are to be glazed, and especially glazed kid, that to conserve their strength neutralization be carefully and thoroughly done. To avoid the above defects one might be tempted to push the neutralization to the limit, up to complete disappearance of an acid reaction. Over neutralization however is just as bad; any excess of alkaline salts combines with the hide with a vitrefying action upon drying which renders the leather hard and flat despite a normal chrome and grease content.

Neutralization should be done with carefully determined quantities of material, which evidently will vary with the manner of tanning. Directions specifying 2 per cent of borax or 1 per cent of sodium bicarbonate imply a uniform absorption of chromium salts of the same degree of basicity, which seldom if ever occurs. Neutralization should also be complete throughout the hide which can only happen when sufficient time has been given for complete penetration. Consequently neutralization should require as much time as the tanning, and if it has been found that 5 hours are needed for the chrome liquors to strike through then neutraliz-

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ing will require 5 hours. The neutralizing agent should be added in portions. Failure to observe these precautions will produce the double defects of an incompletely neutralized center streak with over-neutralized outer surfaces.

Certain tanneries obtain good results by simply washing in water. This is explained by the fact that in many sections the water is in reality a very dilute solution of bicarbonate of lime. Using sufficient quantities of this water excellent results can be obtained and furthermore without danger of over neutralization, since the hide is indifferent to the bicarbonate of lime, the latter acting only as an alkali in the presence of acids.

R. W. F.

A Microbic Damage on Sheepskins for Glove Making. By P. Huc. *Halle aux Cuirs,* Nov. 20, 1921, 346-8. In the tanning of sheepskins for gloves there occurs at times very persistent, dull, more or less deep stains which render the skins unfit for any fancy or light finishes. The skins receive an artificial and a bran bate and are then tanned with alum. The defective skins appear all right until drying commences; when about half dry, the pale characteristic stains show up and become deeper and deeper until when dry they are indelible. From these stains the *bacillus megatherium* has been isolated, which has also been found in certain defects mentioned by Eitner. A ready explanation for this is found in the location of the tannery which is downstream from two confectionery establishments. The *bacillus megatherium* develops splendidly in infusions of fruit seeds, gluten and starch, and these confectionery shops thus provide an excellent culture medium for contaminating the tanning vats. In the bran bate the bacilli find an excellent medium for prolific development which continues in the tanning and appears as stains on drying. This explains the observations of Meunier, that at regular intervals these stains appear in some tanneries and often when using a bran bate. Experiments to prevent this defect using 1 to 10 solution of "aniodol" at the rate of 500 grams per 200 kgs. of tan liquor have proved successful. The plumping is slightly greater and the drying is a little longer, but in no case when the antiseptic was used were the stains observed. It has also been noticed that the stains have a tendency to develop more when the tanning has not been sufficiently prolonged. There are indications that increasing the proportion of alum will prevent the development of these stains.

R. W. F.

The Influence of Formaldehyde on the Ability of Animal Hide to Absorb Acid and Alkali. By A. Gerngross. *Coll.*, 620, 489-491 (1921). Treatment with formaldehyde was found by Stiasny to decrease the amount of acid which hide powder could adsorb, but Moeller has questioned this finding. Gerngross found by color measurements that formaldehyde did decrease the adsorption of dyes. This action of the formaldehyde may either be physical, such as causing a decrease in swelling or coating the

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fibers with polymerized formaldehyde or it may be chemical, in which case there should be an increase in the amount of alkali which treated hide powder will adsorb. The author with H. Lowe determined the adsorption by hide powder of sodium, potassium, barium, and calcium hydroxides, in the presence and absence of formaldehyde. In every case the adsorption followed Freundlich's law and the treated hide powder adsorbed much more alkali than the untreated. The ions, from isohydric solutions, were adsorbed in the order, Ba, Ca, Na, K and the divalent ions were much more strongly adsorbed than the univalent. The basic dye methylene blue was also adsorbed more by treated hide powder. Tanning can therefore hardly be an adsorption phenomena in which chemical properties of the hide play no part. Vegetable tannins, which are negatively charged, were also less adsorbed by treated hide powder, although since they are colloidal, equilibrium was not reached until after 40 hours or more. Chrome tannin, which is positively charged, was however adsorbed less by the treated powder. Whether this is due to its colloidal character or to unspecific adsorption has not yet been determined.

I. D. C.

The Influence of the Cannizzaro Reaction in Aldehyde-Tanning. By W. MOELLER. *Zeitsch. für Led. und Gerb. Chem.*, 1, 54 (1921). The supporters of the chemical theory of tanning have concluded from the apparently lowered adsorption of acids by aldehyde leather that the basic groups of the collagen are saturated by the aldehyde and that hide treated with aldehyde must therefore combine chemically with less acid than untreated. The author advances three causes for the apparent lowering of the adsorption power for acids of hide treated with formaldehyde, as follows:— (1) The formic acid content of commercial formaldehyde was not considered. (2) The cleavage products of hide form methyleneamino acids with aldehydes. (3) The Cannizzaro reaction is catalytically liberated through contact of the formaldehyde with hide and leads to the formation of formic acid.

When 100 cc. of exactly neutralized 4 per cent formaldehyde was mixed with 4.4 grams dry hide powder and allowed to stand 24 hours it required 1.1 cc. N/10 NaOH to neutralize it. Ten portions of 100 cc. each of 30 per cent formaldehyde, exactly neutralized, were allowed to stand and titrated after different intervals of time. After one day the acidity was equivalent to 0.9 cc. of N/10 NaOH and after 25 days, 1.3 cc. This indicates that the Cannizzaro reaction takes place to a small extent merely through the catalytic action of the salts formed in the neutralization according to the following equation:

$$2\ R{:}CHO = R{:}CO{:}O{:}CH_2R + H_2O = R{:}COOH + R + CH_2OH.$$

Further 100 cc. of neutralized, 40 per cent formaldehyde was mixed with 4.5 grams of animal charcoal and allowed to stand 24 hours. The total acidity after this time was equivalent to 5.4 cc. N/10 NaOH and

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the acidity of the original charcoal in distilled water was equivalent to 3.1 cc. which designated that sufficient acid was formed through the Cannizzaro reaction to be equivalent to at least 2.3 cc. N/10 NaOH.

In order to demonstrate that the apparent diminution of acid absorption by hide treated with formaldehyde is not due to the saturation of free basic groups by the formaldehyde, experiments were carried out according to the method used by Stiasny and Gerngross substituting animal charcoal for hide powder. With animal charcoal there could be no question of basic groups and still the same difference is noted in the apparent adsorption of acid with and without the presence of formaldehyde which is obtained with hide powder. The results obtained after correcting for the original acidity of the charcoal were as follows:—

Acid adsorption from 100 cc. of solution by 4.5 grams animal charcoal cc. N/10 HCl.

Concentration of HCl	N/100	N/20	N/10	N/2
Without formaldehyde	3.10	8.30	11.25	32.6
With 10 cc. formaldehyde	0.65	5.50	7.45	28.5

It is also shown that the apparent absorption of caustic soda from dilute solution by hide powder is increased in the presence of formaldehyde which is attributed to the formation of acid by the same reaction. When using animal charcoal as adsorbent for caustic soda in dilute solution, there is an apparent decrease in the amount of caustic soda adsorbed in the presence of formaldehyde. This is attributed to aldol-condensation and the preferential adsorption of the polymers formed because of their colloidal nature.

G. W. S.

The Swelling of Gelatin in Aqueous Solutions of Organic Acids. By A. Kuhn. *Kolloid chem. Beihefte*, **14**, 148 (1921). That certain animal substances swell more in acids than in water was first mentioned by V. v. Ebner and O. Hammarsten. The phenomena of the swelling of gelatin in acid and alkali was first investigated quantitatively by Wo. Ostwald in 1905. By the weight method with gelatin plates Wo. Ostwald found the following relation between concentration of acid and the amount of solution absorbed;— At N/210 a minimum, at N/26 a maximum after which the curve fell quickly at first and then slower. From this investigation it could also be concluded that acids of the same strength, such as, hydrochloric, sulfuric and nitric did not swell to the same degree and that the swelling action of sulfuric was exceeded by the much weaker acid, acetic. A difficulty was encountered in the exact determination of the maximum because the gelatin plates became very soft, were easily broken and contained cracks. The volume method used by M. H. Fischer is considered more exact in which the swelling substance is used in powdered form and its increase in volume taken as a measure of the swelling. Reference is made to the work of J. Paessler and Appelius, Eitner, Stiasny, and McLaughlin on the swelling of hide. H. R. Procter determined the acid swelling of gelatin by a modified

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weight method. He confirmed the results of Wo. Ostwald, in particular for hydrochloric acid but based on the titrimetric determination of the amounts of acid taken up by the gelatin he arrived at a different conclusion. He assumed that the difference between titrations in the presence of gelatin using phenolphthalein and methyl orange as indicators, indicated the amount of acid that was chemically combined and this he called fixed acid. The fact that in swelling, in hydrochloric acid in particular, a part goes "into solution" and should also be given consideration was not considered. The difference between firmly and less firmly combined acid can probably be traced to the so-called "protein error." Procter could not observe a maximum with acetic and lactic acids while he states that in stronger concentrations the gelatin is dissolved. A maximum must occur at the point where solution exceeds the swelling, and such has been established for all acids used in the author's work with the exception of a few difficultly soluble acids.

Kubelka determined the absorption of organic acids by hide powder by the weight method and by titration and confirmed the validity of the adsorption formula for organic acids. From the order of the first four acids of the fatty acid series he concluded that the dissociation constants are a decisive factor in adsorption. W. Moeller investigated experimentally with hide powder the relation between hydrolysis and adsorption. He calls attention to the fact that the apparent acidity obtained with various indicators when titrating an acid solution which has been in contact with hide powder for one hour differs from the actual acidity because of the so-called protein error. In the swelling of gelatin, hydrolysis is much greater than with the more resistant hide powder.

The extraordinarily large time variability of internal friction that gelatin solutions possess precludes the use of gelatin solutions for studying the swelling phenomena by viscosity measurements. Nevertheless more simple protein solutions serve such as serum albumin which was investigated by Wo. Pauli and H. Handovsky in the presence of organic acids. Analogous to swelling there was found an increase in viscosity with increase in acid concentration and then a sharp decrease, a complete parallelism with the results of Wo. Ostwald even in the position of maxima. The acids arrange themselves neither in reference to the maximum viscosity nor in reference to the steepness of the rise in viscosity, according to their strength expressed by the dissociation constants. Wo. Pauli considers that this supports the assumption that the taking up of acid by protein is a pure chemical or electro chemical process analogous to salt formation.

J. Traube and F. Kohler used the rapidity of gelatinization to investigate the swelling phenomena. Their results were entirely analogous to those of Wo. Ostwald, M. H. Fischer and Wo. Pauli. With increasing concentration of acid a retardation of the time for gelatinizing up to

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a maximum after which, with increasing concentration, there was again a falling off. Here also an arrangement of acids according to their strength showed nothing.

In the individual work of the author the volume method of determining swelling was accepted as more accurate than the weight method. The error in this method increases somewhat with the increase in height due to swelling. In the region of pure swelling (where the swelling is not too strongly affected by hydrolysis) up to about 50 mm. increase in height the error is within ± 1 per cent and increases with increasing swelling so that at the maximum figures obtained in this work it is ± 2 per cent. After exceeding the maximum this method is inexact. All experiments were run at least in duplicate and the average result taken. So that the method is considered sufficiently exact for the relative measuring of the swelling process. Powdered commercial gelatin was used throughout. Preliminary comparative tests using oxalic acid with commercial gelatin and pure "glutin" prepared by the method of E. T. Mörner [*Zeitschr. f. phsiol. Chem.* **28**, 471 (1898)] gave practically no difference in swelling power. Most of the acids used were Kahlbaum preparations, all of which were tested for purity by boiling- and melting point determinations. It was necessary to redistill or recrystallize in the majority of cases.

The method used consisted of introducing a weighted amount (0.200 gr.) of powdered gelatin into a test tube with 20 cc. of liquid, shaking from time to time and after settling of the swollen particles the height of swelling was read from a support having millimeter graduations. The gelatin used for all experiments had an average diameter of 0.0150 cm. which was obtained by sieving. Larger particles gave an upper edge that was not sharp thus making readings difficult while finer particles gave lower results on account of greater hydrolysis. The customary glass tube was used (160 x 15 mm.). All tubes were numbered, standardized and corrected in terms of a normal tube. All swelling experiments were conducted in a thermostat at 20° C. for 72 hours. 20° was taken as the optimum temperature for swelling as was demonstrated by comparative tests with formic acid at temperatures of 0°, 16°, 20° and 22° C. At a temperature of 20° maximum results were obtained for swelling. The results obtained at 22° were intermediate between 16° and 20°. The acid concentration at which the maximum swelling for each temperature occurred was different. Seventy-two hours was taken as the time for the swelling because comparative experiments at 24, 48 and 72 hours showed an increase in swelling at 48 hours over 24 hours and at 72 hours over 48 hours although the maximum swelling was obtained at a higher acid concentration the shorter the time period. Thus for acetic acid the maximum swelling was obtained for a 72 hour period at an acid concentration of 0.2 N, and an increase in acid concentration beyond this showed a sharp drop; for a 48 hour period the maximum was obtained at 0.5 N, which was followed by a sharp drop, while

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for a 24 hour period the swelling apparently continued to increase up to a concentration of 1.0 N. Such was found to be typical for all acids investigated and is accounted for by an increase in hydrolysis with increase in time of contact, just as the swelling increased, which causes the point of maximum swelling to occur at the lower concentration. The progress of hydrolysis with the swelling has been difficult to observe with the relatively large gelatin disks used in most cases while it is easily discernible in this case because of the rapidity of solution when such a large surface is presented as represented by the fine powder. It is also seen that a swelling equilibrium in the narrow sense cannot be claimed. With the small size of the particles as used here it would be assumed that the maximum absorption of liquid would be reached in a very short time, while it is seen that 48 hours gives an increase over 24 hours and 72 hours over 48 hours with every indication that it would increase more with an increase in time.

The swelling producing properties on gelatin of about 50 organic acids by the method outlined above was measured and the results are given in 64 tables and 16 figures. *Aliphatic acids.*—(1) Fatty acid series.—formic, acetic, proprionic, butyric, iso-butyric, valeric, iso-valeric and iso-caproic acids were compared with hydrochloric, nitric and sulfuric acids. The fatty acids arranged in the order of the increasing height of the maximum shows that the maximum swelling is independent of the strength of acid as indicated by the dissociation constant. As an example of the independence of the maximum swelling of the strength the following three acids serve as an example:

	Maximum in mm. swelling height	Dissociation constant 100 k.	Concentration of H+ at maximum in millimol per liter
Hydrochloric	91.7	∞	10
Formic	105.5	0.0214	9.25
Acetic	99.7	0.0018	1.74

(2) Hydroxy acids.—Glycolic acid and commercial and a pure lactic acid were investigated. Weak maxima were characteristic of both of these acids of this type. The weak maxima are explained by the lower hydrolysis of gelatin in spite of the great swelling action.

(3) Halogen substituted fatty acids.—Mono, di- and tri-chlor acetic acids and monobrom- and monocyan-acetic acids were used. Here also it is seen that the strength of the acids has nothing to do with the amount of swelling but it is apparent that the strongest acid gives its maximum at a lower concentration of acid and may be arranged in this order.

(4) Dicarboxylic acids.—Oxalic, succinic and malonic acids were investigated. With these acids it was also found that the relative amount of swelling was independent of the strength of the acids but that the strongest acid gave its maximum at the lower concentration.

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(5) Polybasic hydroxy-acids.—Tartaric, citric and malic acids were investigated.

(6) Unsaturated acids.—Fumaric and maleic acids were used as examples. Maleic acid with a dissociation constant of 100 k = 1.17 has a somewhat greater maximum (108.1 mm.) than the weaker fumaric acid (100 k = 0.093) with a maximum at 106.1 mm. This is one of the few cases where the stronger acid also has the greater maximum. The relation of the relative strengths of the acids to the concentration at which the maximum occurs as noted for all previous examples also holds with this type of acid.

(7) Glycochol.—As a final example of the aliphatic series this amino acid was used and showed properties worthy of note. At concentrations below 0.05 N, glycochol only increases the swelling a very little above pure water. At 0.05 N it is about equal to pure water and with increasing concentration there is a steady depression of swelling. Its action is very similar to that of a pure salt.

Aromatic Acids.—With a few exceptions maxima could not be obtained with acids of this class because of their low solubility. (1) Monocarboxylic acids.—Benzoic, m-toluic and phenylacetic acids were used as types.

(2) Hydroxy acids of the monocarboxylic series.—Salicylic, m-hydroxy-benzoic and mandelic acids were used. The latter is the only one whose solubility was great enough to give a swelling maximum.

(3) Sulfonic acids and derivatives.—Benzene-sulfonic and sulfanilic acids were used. Benzene-sulfonic acid which is a stronger acid than sulfanilic gave its maximum swelling at a lower concentration. Comparison of the results with benzene-sulfonic acid with those of the mineral acids shows that the former is a stronger hydrolyzing agent than the latter as the maximum was obtained for benzene-sulfonic acid at a concentration of 0.0086 N while each of the mineral acids gave their maxima at 0.01 N. The gelatin was completely dissolved in a concentration of 0.173 N benzene-sulfonic acid. It is also worthy of note that benzene-sulfonic acid gave greater values for swelling than did the mineral acids.

(4) Unsaturated monocarboxylic acids.—Cinnamic acid was used as a type.

(5) Dibasic acids.—Phthalic acid was used.

(6) Polybasic phenolic acids.—Protocatechuic and gallic acids and tannin were investigated. Comparatively great swelling was obtained with the first two although maxima could not be obtained within the limits of solubility. The action of tannin was investigated in very dilute solution. In the concentration of 0.005 N the swelling increases with the time as for acids. At 0.001 N after 48 hours there is no longer an increase with time. At 0.002 N the swelling falls with increase in time. Up to 0.02 N the swelling after 24 hours is still greater than the water value. For the time period of 72 hours the swelling in tannin solution

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is greater than in water up to a concentration beyond 0.002 N, after this it falls rapidly.

(7) Phenols.—Relations very similar to the above were observed with phenols because they are of acid character even though very weak. Picric acid which is one of the strongest organic acids (100 k = 16) is also a well known protein precipitant. Both of these characteristics are demonstrated. In the lower concentrations up to 0.01 N it acts as a pure acid. There is a steep rise in the swelling curve up to a definite maximum at 0.005 N and then the gelatin begins to be decomposed. From this point the swelling falls sharply to the water value at 0.01 N concentration. In concentrations between 0.01 N and 0.0125 N gelatin is still dissolved but at the same time the solution is weakly coagulant as the solution over the gelatin is turbid. From this point to 0.05 N the swelling action is entirely overcome by the coagulating action. Gelatin is no longer dissolved and the solution remains clear. Phenol shows a corresponding action although it increases the water swelling but little. Pure water gave a swelling value of 41.6 mm.; phenol gave a maximum swelling of 48 mm.; picric acid gave a maximum swelling of 88 mm. The dihydroxyphenols, hydrochinon, resorcin and pyrocatechin give entirely similar results with the exception that the reversal from swelling to coagulation occurs at a somewhat lower concentration (about 0.17 N against 0.30 N for phenol). They are stronger in their coagulating action and correspondingly weaker in their swelling action than phenol. Finally, α-naphthalene-sulfonic acid was investigated on account of its connection with the coagulating action of these compounds. It gave similar results to those for picric acid—an increase in swelling up to a maximum at 0.1 N and then a sharp fall due to hydrolytic action. Between 0.02 N and 0.05 N coagulation occurs sharply without showing a turbid solution.

The maximum amounts of liquid absorbed by gelatin in the presence of mineral acids can be very different for each. With organic acids the absolute difference in swelling maxima are often inconsiderable while an important difference in the general form of the swelling curve arises. The swelling maximum is not a constant which is specific for the swelling action of an acid. An attempt was made to find such constants which were independent of the concentration and which indicated plainly the specific swelling ability. It was found that the exponential formula of the form $x = q.c^n$ closely approximated swelling especially at the lower concentration. x indicated the amount of swelling liquid taken up, q and n specific constants and c the acid concentration. Substituting the swelling height for the amount of liquid absorbed the formula served for the important increasing arm of the swelling curve and q and n were determined for all of the acids investigated. q is designated as the "specific swelling height" and n as the "specific increase in swelling." The following table gives the data for the acids investigated.

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Acid	Constants of the swelling equation q	n	Height of maximum in mm.	Concentration for maximum swelling in N	Dissociation constant 100 k.
Hydrochloric	56.3	1.055	91.7	0.01	∞
Nitric	60.0	0.965	93.4	0.01	∞
Sulphuric	54.9	0.780	78.5	0.01	∞
Formic	72.8	0.467	105.5	0.05	0.0214
Acetic	40.9	0.878	99.8	0.2	0.0018
Proprionic	39.8	0.655	100.8	0.4	0.0013
Butyric	39.4	0.803	98	0.4	0.0015
Iso-butyric	37.6	0.838	97	0.4	0.0016
Valeric	35.7	0.924	——	——	0.0016
Iso-valeric	44.3	0.899	120	0.4	0.0017
Iso-caproic	37.1	0.930	——	——	0.00145
Glycolic	49.4	1.125	103.4	0.3	0.01526
Lactic	50.5	0.864	96.2	0.32	0.0138
Lactic (techn.)	——	——	90	0.2	——
Chloracetic	53.8	1.17	98.5	0.05	0.155
Dichloracetic	85.9	0.435	104.9	0.01	5.14
Trichloracetic	50.5	1.579	97	0.01	30
Bromacetic	54.1	1.198	100.5	0.05	0.138
Cyanacetic	61.2	1.130	99	0.02	0.370
Oxalic	——	——	114	0.02	3.8
Malonic	53	1.316	109	0.05	0.158
Succinic	46.6	0.891	——	——	0.00655
Malic	45.6	1.152	105.3	0.1	0.04
Tartaric	54.8	1.052	105	0.05	0.097
Citric	50.1	1.062	105.5	0.09	0.087
Maleic	49.1	1.415	108.1	0.02	1.17
Fumaric	46.3	1.440	106.1	0.04	0.093
Benzoic	54.5	0.902	(92.9)	(0.02)	0.0065
M-toluic	55.6	0.548	(68.5)	(0.0067)	0.0056
Phenylacetic	51.6	0.975	(98.9)	(0.033)	0.0053
Salicylic	57.3	1.458	(101.1)	(0.011)	0.108
M-hydroxybenzoic	53.8	0.995	(97.5)	(0.06)	0.0083
Mandelic	69.2	0.682	104.6	0.02	0.0430
Benzene-sulfouic	56.8	1.739	105.9	0.0086	20
Sulfanilic	61.9	0.994	104.8	0.025	0.062
Cinnamic	43.6	0.855	(60.3)	(0.003)	0.0038
Phthalic	45.7	1.532	(103.1)	(0.066)	0.0126
Protocatechuic	46	1.083	(120)	(0.1)	0.0033
Gallic	49.3	1.048	(120.1)	(0.05)	0.0091
Tannin	——	——	47	0.001	——
Picric	58.7	1.289	88.6	0.005	16
Phenol	——	——	48	0.10	1.3×10^{-8}
Hydrochinon	——	——	46.3	0.10	1.1×10^{-8}
Resorcin	——	——	43.7	0.05	3.6×10^{-8}
Pyrocatechin	——	——	49.6	0.10	3.3×10^{-5}
α-napthalene-sulfonic	58.1	1.95	102	0.01	27

NOTE:—The figures in parenthesis designate the results with saturated solutions when solubility was too low to obtain maxima.

There is no general connection between the q and n values, between the q value and strength of acid nor between the n value and strength of acid, nor between any of these with the maximum swelling. The author describes swelling as the result of four simultaneous processes. Of first importance is (1) true swelling (hydration), (2) simultaneous peptization (sol-formation), (3) hydrolysis, (4) dehydration or coagula-

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tion. The first predominates at low concentrations, the effects of the others increase with increasing concentration in the order in which they are numbered. Maximum swelling is defined as that point at which swelling, which increases with increasing concentration, is exceeded by sol-formation and hydrolysis which likewise increase. There is no relation between the magnitude of the maximum swelling and strength of acids but there is a relation between the strength of acids and the concentration at which maximum swelling occurs. For strong acids the maximum swelling occurs at low concentration values, for weak acids at higher concentrations and acids of intermediate strength fall between the two extremes.

The results conclusively indicate that acids act on gelatin in such a way that at low concentrations a specific increase in hydration occurs, whether a chemical or adsorption compound is formed still remains undecided. At higher concentrations peptization and (chemical) hydrolysis occur, followed by dehydration and coagulation which work against the swelling process. G. W. S.

PATENTS

Leather-working Machines. British Patent 168,155. H. SPRUCE and J. LEATHWOOD, both in Runcorn, Cheshire. May 27, 1920, No. 14416. The usual roller in butt rolling machines is replaced by a non-rotary burnishing tool in the form of a triangular prism, slightly cambered from end to end and with rounded corners, these constituting the burnishing-surfaces. The supporting-spindle is normally locked to prevent rotation but may be released to bring a fresh surface into operation.

Apparatus for Manufacturing Glue. U. S. Patent 1,401,965. H. CROWELL, Brooklyn, N. Y. Filed April 25, 1917, Serial No. 164,360. Renewed March 10, 1921.

Utilization of Wastes or Scraps of Leather. U. S. Patent 1,402,085. M. NAKAYAMA and K. ADACHI, Tokyo, Japan. Filed Oct. 1, 1920. A leather fabric composed of a series of strips interwoven with each other, each strip consisting of a series of pieces of leather arranged end to end and connected together, and the points of connection of the pieces of each strip being concealed beneath the pieces of the other strips.

Tanning Composition. U. S. Patent 1,402,283. R. B. COCK, Gomshall, England. Filed Oct. 31, 1918. A composition for the tanning of hides, comprising hyposulphite of soda, aluminum sulphate, and vaseline in the approximate proportions by weight respectively of 1.5, 1 and 0.5, and a mixture of glycerine, tanning extract, and turpentine in the approximate proportions by measure respectively of 1, 2000, and 1.

Process for Tanning Leathers and Skins. U. S. Patent 1,204,633. H. MORIN, St.-Denis, France. Filed Dec. 6, 1916. A process of tanning skins wherein the skin is steeped in an alkaline silicate solution, afterwards treated by a silicate decomposing agent and then impregnated with brine and rinsed and dried.

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Process of Chrome Tanning. U. S. Patent 1,404,957. F. HIRSCH, Vienna, Austria. Filed Mar. 5, 1914. A process of chromic tanning consisting in subjecting the hides to a treatment with chromic acid and reducing the latter by stoichiometric mixture of bisulphite of soda, and a neutral salt of aluminum; or mixtures of bisulfite of soda and a basic salt of aluminum or bisulfite and sulfite of soda and a neutral salt of aluminum.

Method for the Treatment and Utilization of Scrap or Waste Leather. U. S. Patent 1,405,600. S. C. LANSDOWN, Melbourne, and B. MAGNUS, North Fitzroy, near Melbourne, Victoria, Australia. Filed Oct. 14, 1918. An improved method of and means for the treatment and utilization of scrap or waste leather consisting of reducing the same to a coarse powder, cleansing the powdered leather with oxalic acid, adding thereto an adhesive and drying composition consisting of liquid glue, boiled linseed oil, carbolized oil and oil of cloves.

Leather-Working Machines. British Patent 170,924. TURNER TANNING MACHINERY CO., LTD., London, and F. C. HOEFLING, Bramley, near Leeds. July 28, 1920. Relates to buffing and like leather-working machines.

Tanning Materials. 171,136. A. ROMER, Heidehofstrasse, Stuttgart, and DEUTSCH-KOLONIALE GERB. & FARBSTOFF GES., Phemhafen, Karlsruhe, both in Germany. July 7, 1920, No. 19154. Waste sulphite-cellulose lye is treated with lime or calcium carbonate to neutralize the acids, and is separated from the precipitate. The calcium is then precipitated by alkali compounds such as sodium carbonate or silicate. Hydrochloric, sulphuric, or other acid is added to the resulting solution of sulpho-lignates in amount equivalent to 50-100 per cent of the alkali used in precipitation. The liquid can then be used for tanning. Instead of acid, there may be added salts of metals such as are used in mineral tanning, for instance aluminum, iron, or chromium chloride; the liquids thus obtained can be used directly for tanning. The liquid may be fermented after the addition of the lime or calcium carbonate, and may be concentrated by evaporation after the treatment with the alkali compound.

Tanning. 171,693. GERB-UND FARBSTOFFWERKE H. RENNER and CO., AKT.-GES., 20, Billhorner—Canalstrasse, Hamburg, Germany. Nov. 15, 1921, No. 30484. A process of tanning consists in treating the hide with an arsenic compound which, if insoluble in water, has been rendered soluble or colloidal. In one example, a tanning-agent is prepared by adding to a suspension of an insoluble compound of arsenious, arsenic, sulpharsenious, sulpharsenic, phenylarsinic, or diphenylarsinic acid or arsenophenol a sufficiently large proportion of an alkali salt to produce a colloidal solution. In another example, the hide is treated with a free organic sulphonic acid of a hydrocarbon or with a synthetic tannin-agent obtained by

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condensation and sulphonation of a phenol and hydrocarbon used as a solvent for an arsenic compound, particularly a heavy metal salt of arsenious or arsenic acid.

Synthetic tanning-agents. 171,729. A. G. BLOXAM, London.—(*Gerb-und Farbstoffwerke H. Renner & Co., Akt.-Ges.; 20, Billhorner-Canalstrasse, Hamburg, Germany.*) June 24, 1920. *Sulphonic acids.*—Tanning-agents are obtained by sulphonating the resinous condensation products prepared from phenols and formaldehyde with the aid of basic condensing-agents. Starch, sugar, glucose or materials containing them, may be mixed with the parent materials, or the resins before the sulphonation The sulphonation may be carried out so as to yield either readily-soluble products or products which are sparingly-soluble or insoluble. The readily-soluble products have the property of solubilizing the sparingly-soluble products, or the unsulphonated resins, or the insoluble phlobaphenes contained in vegetable tanning-agents, and the resulting colloidal solutions may be employed as tanning-agents.

Synthetic resins; synthetic tanning-agents. British Patent 171,956. ELEKTROCHEMISCHE WERKE GES., Berlin, and H. BOSSHARD, and D. STRAUSS, Bitterfield, Germany. Jan. 10, 1921. A resinous condensation product is obtained by heating naphthalene with glycollic acid or glycollide and an acid reagent such as phosphorus pentoxide in an autoclave at 130-170° C. The product has properties similar to those of shellac, and on sulphonation produces a synthetic tanning-agent.

Recovering Fats and Soaps from Wash Liquors. British Patent 172,012. J. DUCLAUX, Paris. Nov. 22, 1921. Washing-waters, especially those used for washing wool, are treated by ultra-filtration through a membrane under pressure in order to separate substances in solution or suspension. The membrane may be of collodion, denitrated collodion, or cellulose precipitated from a cupro-ammoniacal solution. The mineral salts and alkaline salts of lower fatty acids pass through the membrane, while the fatty acids and their alkaline-earth salts, and the insoluble organic elements of the suint, remain behind. The filtrate may be re-employed for washing, and again filtered. Soapy waters, before being used for washing, may be similarly filtered to remove excess of fatty acids. The filter cake may be extracted from the filter by reversal of pressure, and the filter then regenerated by washing with dilute acids, alcohol, acetone, or methyl alcohol or acetate.

Synthetic Tanning-agents. British Patent 172,048. A. G. BLOXAM, London.—(*Gerb. und Farbstoffwerke H. Renner & Co., Akt.-Ges.; 20, Billhorner-Canalstrasse, Hamburg, Germany.*) June 25, 1920. Soluble acid resins are obtained by treating coumarone resin or solvent naphtha or "heavy benzole" with concentrated or fuming sulphuric acid. When solvent naphtha is treated, the resulting acid resin is dissolved out by water from the unattacked oil. The products, after removal of free sulphuric acid by alkalis, lime, etc., are used as tanning-agents.

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MAY 8 1922

19th ANNUAL MEETING
BIGWIN INN

VOL. XVII MAY, 1922 NO. 5

THE JOURNAL OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION

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Carter, Clyde, 1136 Broad St., Newark, N. J.

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Tilden, P. S., E. I. du Pont de Nemours & Co., 21 East 40th Street, New York, N. Y.

Wikoff, Allan G., % McGraw-Hill Co., 1570 Old Colony Building, Chicago, Ill.

CORRECTION

In the article on the Official Method of Tannin Analysis on page 160, the second and third items, 0.065 and 0.200, in the first column of the table should read 0.015 and 0.020 respectively.

BUREAU OF EMPLOYMENT

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Notice of positions vacant and situations wanted will be kept on file at the Secretary's office.

Prompt co-operation of the chemists in the trade will result in a mutual benefit to those seeking employment and those desiring chemists.

POSITION WANTED.

LEATHER CHEMIST and SOLE LEATHER TANNER 38 years old. Fifteen years experience. For information address A-100, % American Leather Chemists Association, 22 East 16th Street, New York City.

THE NINETEENTH ANNUAL MEETING
BIGWIN INN, CANADA
June 21st, 22nd, 23rd

Much enthusiasm has been aroused over the innovation in the location for the Annual Meeting which promises well for a record attendance. Bigwin Inn offers inducements that appeal to everyone however remotely interested in matters appertaining to the

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leather trade. First and foremost it is located in a spot richly endowed by nature, wonderful in scenic beauty, while at the same time it offers all the comforts and conveniences that go to make existance pleasant.

In the nature of things our members and our friends in the trade will be thrown into a more intimate relationship than has been possible at any previous Annual Meeting. We will all become better acquainted, richer in the knowledge of many things that such intimacy engenders, and therefore better able to be of service to one another in the future.

The committee in charge of the program is confident, from the response already received, that they will be able to present to the members the most noteworthy program in the history of the Association. Detailed information will be presented from time to time as the program of the meeting becomes more crystallized, but it is possible to announce at this time that Professor F. E. Lloyd, of the Department of Botany, McGill University, Montreal, will address us on "The Mode of Occurrence of Tannin in the Living Cell." This is a subject that has been but little discussed in our Association and one which should be both intensely interesting as well as instructive. Several papers will be presented from the Leather Research Laboratory, the subjects of two of these papers already having been received—"The Science of Curing" and "The Bacteriology of the Fresh Hide." In addition to the special addresses to be delivered, reports will be given by the chairman of our various committees, and discussions will take place relative to new ideas and problems that have come to the fore since our last Annual Meeting.

Furthermore the program committee urges the assistance of the members of the Association to contribute toward the success of the meeting by presenting original papers on any subject no matter how remotely it may have to do with the leather trade. The practical men of the trade who come in contact so much more intimately with the less theoretical problems are urged to present these problems at the meeting, in person preferably or by paper if they are unable to be present.

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Part of the work of the program committee that is well under way has to do with the question of the entertainment of the members and their families. Arrangements have been made for a reception, band concert, bridge tea, dancing, golf, tennis, bowling, swimming, boating, etc.

It is suggested that members who were doubtful whether they could be present at the meeting and those who have stated that they could not and have since changed their mind write to the Secretary to this effect. Appearances indicate that this Annual Meeting is going to be so much of a success that no member can well afford to miss it. Attention is again called to the fact as given in the original circular letter that the hotel rates at Bigwin Inn quoted to the members are enforced for three weeks following the close of the Annual Meeting and the desirability of selecting this time for a vacation is apparent.

A circular letter will be sent to the members later giving specific information as to the details of the program, entertainment, train schedules, railway rates, etc.

H. C. REED
Chairman of Program Committee.

NOTES ON THE DETERMINATION OF ACID IN LEATHER

By J. S. Rogers

Received March 16, 1922

The Procter and Searle method modified according to the recommendation of the 1919 American Leather Chemists Association Committee[1] has been adopted as a provisional method of the American Leather Chemists Association.

Questions have been raised, at various times, as to what and how much effect certain materials used in tanning and finishing leather have upon the percentage of acid found. It was, therefore, thought that the following results might be of some interest to those using this A. L. C. A. Provisional method.[2]

Five samples of leather were used, and the acidities found by the A. L. C. A. Provisional method were as follows:

[1] *J. A. L. C. A.*, 14, 330, 1919.
[2] *J. A. L. C. A.*, 17, 88, 1922.

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	Reaction	Cc. acid req.	Per cent acid as H_2SO_4
		0.7	
No. 1 cut from two hides		1.0	
out of last layer	Alkaline	1.3	———
		1.3	
		Avg. 1.1	
		1.0	
No. 2 cut from same hides		1.0	
out of extract wheel	Alkaline	1.2	———
		1.2	
		Avg. 1.1	
		0.8	
No. 3 cut from same hides		0.8	
out of tempering layer	Alkaline	1.1	———
		1.1	
		Avg. 1.0	
		Cc. alk. req.	
		2.1	
No. 4 cut from same hides		2.1	
out of bleach	Acid	1.8	
		1.8	
		Avg. 2.0	0.49
		2.2	
No. 5 cut from same hides		2.2	
out of oil wheel	Acid	1.9	
		2.1	
		Avg. 2.1	0.51

The hides from which this leather was made were limed in a liming mixture containing some sodium sulphide. They were not delimed or plumped by any added acid. The tan liquors used contained some bisulphited quebracho extract. The results on sample No. 1 thus show that the sulphur of the hides, sulphides from liming, sulphites and bisulphites from treated extracts, and iron and aluminum salts present in these hides or tanning materials are not responsible for any free acid that may be found later on in samples cut from these hides. In the extract wheel the hides were subjected to the action of bisulphited extracts and sulphonated oil. The results for sample No. 2 show that the bisulphited extract and the sulphonated cod oil are not responsible for any free acid found later on in samples cut from these hides. These results are still further confirmed in sample No. 3 after the leather came out of the tempering layer. The sample cut after the alkali and acid bleach showed 0.49 per cent acid. This shows the first normal place at which acid might be expected under the above tanning conditions. The sample collected after the hides came from the oil wheel

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showed 0.51 per cent free acid. In the oil wheel the hides were oiled with mineral oil and sulphonated cod oil. The acid found was 0.02 of one per cent higher than that obtained on the samples taken immediately after the bleach.

Reference to the American Leather Chemists Association Committee Report on the Determination of Sulphuric Acid in Leather for 1918[3] will show confirmation of some of the results given above. It will be noted in that report that sulphite cellulose extracts show acid by Proctor and Searle method.

It should be mentioned that any direct addition of sulphuric acid in the leather after the bleach will probably show up as free acid in the finished leather.

SUMMARY

(1) These results indicate that hides subjected to the above normal tanning conditions should not show excessive amounts of free acid by the modified Procter and Searle method or by the new Provisional A. L. C. A. method.

(2) These results show that the sulphur from the hide, sulphides from liming, iron and alumina from hides, limes, and tanning materials, and the sulphites and bisulphites from bisulphited extracts do not show up as free acid by the A. L. C. A. method.

(3) These results show that use of sulphonated oil results in practically no increase in the per cent of acid found by the A. L. C. A. method.

(4) The results show that the alkali and acid bleach is responsible for practically all of the free acid found by the A. L. C. A. method in this leather. Further they show that the amount of such free acid does not run abnormally high when the leather is not subjected to some further treatment with acidic materials.

THE COLOR MEASUREMENTS OF TANNIN SOLUTIONS —COMMITTEE REPORT

T. Blackadder, Chairman

Reviewing the work of this committee up to the commencement of this year's work it appeared that a machine based on the known measurable physical properties of light is necessary in order to obtain a reliable standard measure of the color of a

[3] *J. A. L. C. A.*, 13, 319, 1918.

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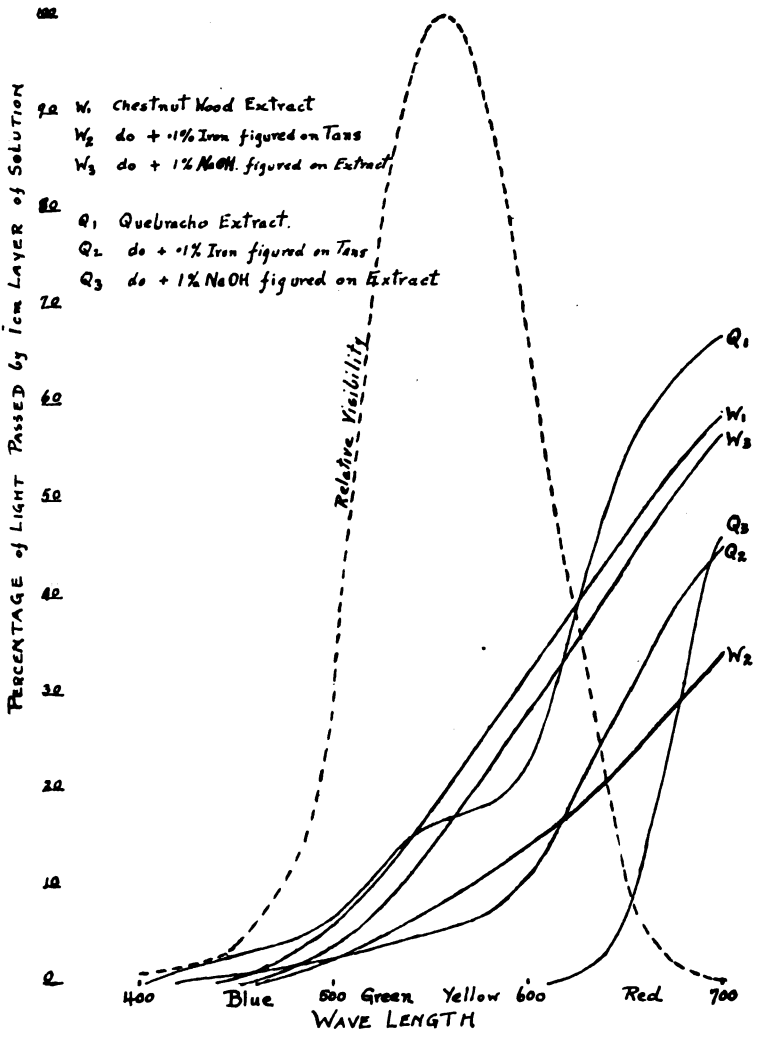
tannin solution. Further it appeared that the use of blue in our standard was unnecessary and misleading. The suggestion was finally made by the chairman that the color of a solution be analyzed spectrophotometrically and the color analysis so obtained be made a basis of future work.

Owing to the nature of the work it has again seemed more advisable to carry on the work in the chairman's laboratory.



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In the analysis of the color of the light transmitted by tannin solutions the Bureau of Standards kindly consented to aid the work of the committee. The curves shown below are a graphical representation of the analysis of the light passed by solutions of quebracho and of chestnut wood extracts. The influence of partly neutralizing the solutions and also of iron contamination is also shown. The curves show the percentage of the incident light passed by a 1 cm. layer of soluble solid solution of analytical strength.

The study of these curves shows in general that the amount of blue light passed is in all cases negligible and that there is a gradual increase in the transmission as we progress towards the red end of the spectrum. A second point to note is the influence of the visibility of the different wave lengths. The visibility curve included in this diagram shows that the visibility is highest in the green and yellow regions of the spectrum. This denotes that a given change in the amount of green or yellow light passed by a solution will have more effect than the same change in any other region of the spectrum.

Among the conclusions to be drawn from these curves it would seem that the measurements of the blue light is superfluous but that the measurement of the green and the yellow is highly important. It would further seem that there is no indication of a sudden change in color due to treatment of the extracts nor is there any special color predominance which might indicate a special advantage of measuring the light transmitted in any narrow band of the spectrum. We can therefore divide our spectrum to suit our practical convenience with the one provision that the green and the yellow regions of the spectrum be included by themselves as two of our subdivisions.

To arrive now at a practical application of the above considerations to the problem of color measurement it would appear that if we can select just such regions of the spectrum as we desire, and observe these each individually we can definitely measure the amount of light passed in each region. This should give us definite set of readings for a given solution. The Hess-Ives machine which was tested by the committee last year operated on this principle and demonstrated that the use of different illuminants was without effect on the readings obtained and also

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that different operators obtained concordant readings. This machine however is rather complicated and it seemed desirable to evolve a simpler method of arriving at the measurements desired without deviating from the principles outlined above.

The problem at this point resolves itself into two—the first phase being the selection of three regions of the spectrum, green and yellow being two and select color filters which will enable us to observe these regions independently. These filters must be such that each includes one defined band of the spectrum and that the three bands include the whole spectrum (less the blue-violet end) without overlapping. The bands finally chosen were

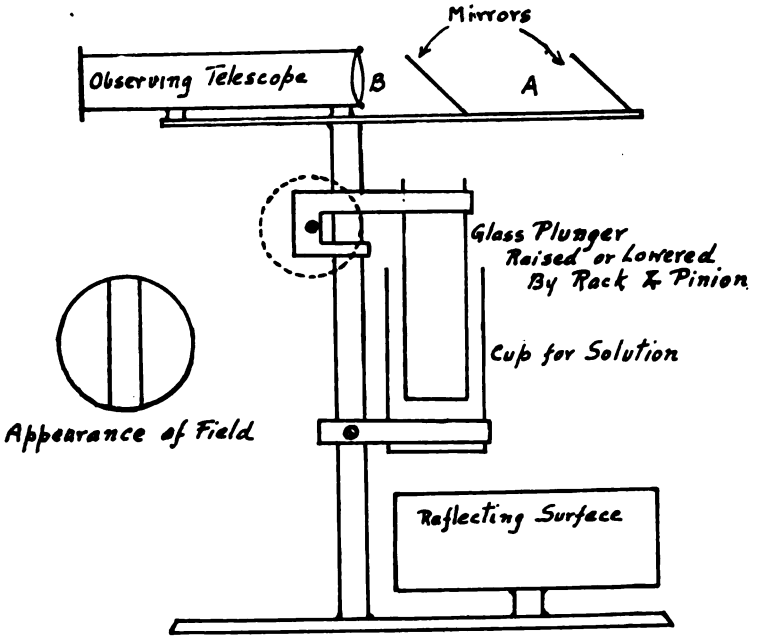

Fig. 1—Light from the reflecting surface travels two paths to the observing telescope. One path leads through the air to mirror *A*. Thence through a neutral grey glass which absorbs one-half of the light to the telescope. The second path leads through the solution in the cup to mirror *B* and thence to the telescope.

The thickness of the solution layer is altered by raising or lowering the plunger.

In order to observe the chosen band in the spectrum the color filter is placed in front of the telescope at *B*.

The mirror *B* is a narrow mirror so that light from mirror *A* can pass on either side of it giving a field appearance as shown in the inset.

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green (wave lengths 500-550), yellow (wave lengths 550-600) and red (wave lengths 600-700).

The second phase is the development of a machine which will be simple both on account of expense and of simplicity of operation. The use of an immersion colorimeter of the type shown in Figure 1 accomplishes all that could be desired in simplicity while still maintaining accuracy. It measures the thickness of solution which passes a given percentage of light. This thickness measure is as specific as the measure of "percentage of light passed" and judging from the amount of work the chairman has done to date, it appears to offer a rather better differentation between two solutions. The thickness measure can be transferred if desired to a percentage measure by applying the law of absorption.

Your chairman believes that the method outlined above offers a simple method capable of giving a definite measure, which can be numerically expressed, of the color of a tannin solution. The apparatus required is comparatively simple and not expensive. It would further appear that the measure obtained would be unaffected by differences in illumination which would ordinarily occur. Except in extreme cases of color blindness the eye of the operator should not affect the readings. These last two points should however be subjected to practical test before adoption of the method.

Your chairman wishes to take this opportunity of publicly expressing his thanks for the courtesy extended and help rendered by the Bureau of Standards in making Spectral analyses and by the Eastman Kodak Company in assisting in the selection of color filters and by the Smethport Extract Company for the loan of colorimeters.

THE RAPID WASHING OF CHROMED HIDE POWDER —1922 COMMITTEE REPORT

F. F. Marshall, Chairman

R. F. Frey read a paper before the 18th Annual Meeting at Atlantic City on the Rapid Washing of Chromed Hide Powder which was published in This JOURNAL.[1] He recommended that further work be done on this subject, the Council subsequently appointed a committee to investigate this method of washing.

[1] This JOUR., 16, 477 (1921).

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The members who participated in the work were Messrs. R. W. Frey and I. D. Clarke, F. H. Small, H. C. Reed, W. K. Alsop and F. F. Marshall, Chairman. The work undertaken is outlined in the following directions of the chairman:— In order to eliminate considerable work no samples will be sent for the Committee on Rapid Washing of Chromed Hide Powder. Each member will make these tests along with and on a part of his regular routine work. All that is necessary will be to start along with the regular hide powder a second lot for the rapid washing. This hide powder should be washed as described by R. W. Frey and I. D. Clarke in the September, 1921 issue of the Journal, page 478, that is—"The chromed hide powder is poured into a bag of linen or other suitable cloth and washed by draining. The cloth may be conveniently supported over a large ring, clamped on a ring stand or a large tripod using clothes-pin clamps for readily fastening and detaching. The same number of washings and the same volumes of water as are specified in the official method are used, but as soon as the water from each washing has practically run through, that is, subsided to the level of the powder in the bag, the powder is squeezed as usual." Then determine the non-tannin on the same solution. (A) With the hide powder with longer washing. (B) With the hide powder which has been washed rapidly.

The results given in the tables of the collaborators are:

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By H. G. Anderson, The Reed Laboratories

Date Analyzed	1/25/22									
Material	Powdered chestnut extract	Liquid oak bark extract	Liquid chestnut extract	Liquid chestnut extract	Liquid oak and hemlock extract	Liquid quebracho extract	Ordinary solid quebracho	Clarified solid quebracho	Sumac	Divi-divi
Total solids	95.21	45.52	45.54	55.50	47.44	46.21	81.18	78.72	49.55	65.60
Soluble solids	91.80	42.31	42.89	54.30	44.87	45.66	71.75	78.63	47.50	61.97
Insolubles	3.41	3.21	2.65	1.20	2.57	0.55	9 43	0.09	2.05	3.63
Non-tannin (official)	31.14	16.48	15.17	20.59	18.28	10.40	7.07	11.33	17.62	19.53
Tannin (official)	60.66	25.83	27.72	33.71	26.59	35.26	64.68	67.30	29.88	42.44
Non-tannin (rapid)	30 85	16.63	15.28	20.63	18.30	10.31	7.15	11.31	17.67	19.66
Tannin (rapid)	60.95	25.68	27.61	33.67	26.57	35.35	64.60	67.32	29.83	42.31

Hide powder moisture (official)	73.5%	Grams used	47.0
Hide powder moisture (rapid)	73.5%	Grams used	47.0
Mgs. blank (official)	5.9		
Mgs. blank (rapid)	5.4		

Date 1/26/22

(Blank: By shaking 200 cc. of water with hide powder. Filter as usual. Evaporate 100 cc.)

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By R. W. Frey and I. D. Clark, Leather and Paper Laboratory

Date analyzed	12-6-21 Powdered chestnut extract	12-6-21 Liquid hemlock extract	12-7-21 Powdered larch extract	12-7-21 Liquid gambier extract	12-8-21 Ord. solid quebracho extract	12-8-21 Liquid sumac extract
Total solids	91.23	50.28	92.17	39.70	83.58	42.72
Soluble solids	87.76	45.17	83.88	37.50	74.86	40.14
Insolubles	3.47	5.11	8.29	2.20	8.72	2.58
Non-tannin (official)	26.22	17.02	37.45	16.09	5.52	18.31
Tannin (official)	61.54	28.15	46.43	21.41	69.34	21.83
Non-tannin (rapid)	26.11	16.96	37.64	16.12	5.71	18.40
Tannin (rapid)	61.65	28.21	46 24	21.38	69.15	21.74

For analysis dated	12-6-21	12-7-21	12-8-21
Per cent moisture—hide powder (official)	74.4	73.6	73.4
Per cent moisture—hide powder (rapid)	73.5	73.5	73.5
Mgs. blank from official washing	4.0	4.6	4.2
Mgs. blank from rapid washing	3.5	4.9	1.8

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By F. F. Marshall, Kistler Leather Co.

Date analyzed	10-28-21	10-28-21	10-28-21	10-28-21	11-20-21	11-20-21	11-20-21	11-20-21	11-20-21	11-20-21
Material	Liquid chestnut extract	Liquid chestnut extract	Mangrove bark	Liquid quebracho clarified	Liquid che tnut extract	Liquid chestnut extract	Liquid hem. bark extract	Liquid oak bark extract	Liquid chestnut extract	Liquid quebracho clarified
Total solids	41.95	48.27	50.51	46.12	48.20	48.43	47.63	48.00	46.73	46.12
Soluble solids	40.98	47.69	48.83	45.88	46.99	47.07	41.76	43.30	46.56	45.88
Insolubles	0.97	0.58	1.68	0.24	1.21	1.36	5.87	4.70	0.17	0.24
Non-tannin (official)	11.94	16.40	11.89	9.92	15.04	14.50	15.08	15.15	16.85	9.92
Tannin (official)	29.04	31.29	36.94	35.96	31.95	32.57	26.68	28.15	29.71	35.96
Non-tannin (rapid)	12.01	16.44	11.75	10.04	15.13	14.60	15.30	15.36	16.87	10.05
Tannin (rapid)	28.97	31.25	37.08	35.84	31.86	32.47	26.46	27.94	29.69	35.83

Hide powder moisture (official) 72.97%. Grams used 46½.
Hide powder moisture (rapid) 73.43%. Grams used 46½.
Mgs. blank (official) 4.6
Mgs. blank (rapid) 3.9
Date 11/30/21.

(Blank: By shaking 200 cc. of water with hide powder. Filter as usual. Evaporate 100 cc.)

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BY. J. E. MCNUTT, ELK TANNING CO.

Material	Ord. queb.	Liq. chest ext.	Liq. hem. ext.	Mangrove bark	Valonea beard
Non-tannin (official)	6.23	13.96	12.62	11.80	15.55
Non-tannin (rapid)	6.11	13.91	12.56	11.56	15.57

Hide powder moisture (official) 73.25%
Hide powder moisture (rapid) 73.20%
Mgs. blank (official) 4.8
Mgs. blank (rapid) 4.8

Grams used wet 47, ab. dry 12.57
Grams used wet 47, ab. dry 12.59

Date 4-12-1922

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By V. J. Mlejnek, Graton and Knight Manufacturing Co.

Date analyzed / Material	12-8-21 Sulphited quebracho	12-8-21 Oak bark extract	12-8-21 Oak bark extract	12-8-21 Oak bark extract	1-19-22 Chestnut extract	1-19-22 Oak bark extract	1-19-22 Chestnut extract	1-19-22 Chestnut extract	1-19-22 Oak bark extract	1-19-22 Chestnut extract
Total solids	39.60	45.74	48.01	46.99	37.56	45.18	38.15	40.64	47.59	44.44
Soluble solids	39.49	43.23	45.93	44.52	36.37	42.73	37.37	39.51	45.72	41.42
Insolubles	0.11	2.51	2.08	2.47	1.19	2.45	0.78	1.13	1.87	3.02
Non-tannin (official)	4.22	18.03	18.08	16.63	12.57	17.54	12.61	13.35	20.19	13.72
Tannin (official)	35.27	25.20	27.85	27.89	23.80	25.19	24.76	26.16	25.53	27.70
Non-tannin (rapid)	4.13	17.86	17.76	16.43	12.71	17.72	12.96	13.58	20.49	14.08
Tannin (rapid)	35.36	25.37	28.17	28.09	23.66	25.01	24.41	25.93	25.23	27.34

	12-8-22	1-19-22	
Hide powder moisture (official)	72.2%	72.1%	Grams used 47
Hide powder moisture (rapid)	71.9%	73.5%	Grams used 47
Mgs. blank (official)	3.9		
Mgs. blank (rapid)	1.8		

Date 1/25/22

(Blank: By shaking 200 cc. of water with hide powder. Filter as usual. Evaporate 100 cc.)

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COMMENTS

Messrs. Frey and Clarke made the following comments:— "These results confirm those previously published by us, as they show no significant difference between rapid washing and official washing of the hide powder. We are decidedly in favor of rapid washing as it not only saves considerable time but to us is more convenient."

MR. W. K. ALSOP:— "The results are practically the same and in my opinion the rapid method of washing the hide powder is just as satisfactory as the other."

CHAIRMAN:— "The differences found by the two methods are but slight, and we would recommend changing the Official Method of Tannin analysis, Section 12-A Non-Tannins, to include the method for Rapid Washing of Hide Powder."

SAMPLING OF LEATHER FOR CHEMICAL ANALYSIS*

By R. C. Bowker and E. L. Wallace

Received April 19, 1922

It has been recognized for a long time that some parts of a hide are looser fibred than others and consequently will absorb a greater amount of tanning and filling materials, causing thereby a considerable variation in the composition of the finished leather. As a result of this fact, the usual method has been to take a composite sample made up of cuttings from several locations, in order that the chemical determinations might be representative of the leather unit involved. It has been customary, at least in specification work where leather is purchased in the form of backs, bends, or sides, to specify that the sample shall consist of one cutting from each of the back, butt, and belly portions. Although no attempt was made to define the exact location of each of these cuttings it was generally understood that the back cutting should be taken on the backbone edge near the shoulder, the butt cutting from the butt near the tail, and the belly cutting from the center of the belly edge.

The matter of sampling has been treated with considerable detail by a committee appointed by the American Leather Chemists' Association. The report of this committee, published in the August, 1921, number of This JOURNAL, presents a large amount of data showing the variation in the chemical constituents

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for different locations on the hide. From these data the committee has shown diagramatically[1] the locations from which cuttings shall be taken in order to secure a representative sample from either a belly, shoulder, bend, butt, or side.

Considerable analytical work has been done at the Bureau of Standards in connection with sole leather investigations to show the variation in the distribution of the chemical constituents in leather. The sole leather was furnished in single bends and it is considered that the A. L. C. A. Committee on Sampling and others will be interested to note the results obtained by applying the recommended method of sampling for single bends to our data. The results of such a comparison are given in the following tables, which it is believed are self-explanatory. The average values given in the tables may not represent accurately the average analysis of the bends since not all of the pieces were either of the same size or weight, but in view of the fact that all of the pieces were very nearly of the same size it is probable that the figures are very close to the average analysis.

TABLE I.—DATA ON CHEMICAL ANALYSIS OF SOLE LEATHER BENDS DESCRIBED IN TECHNOLOGIC PAPER NO. 138

	Lot A		Lot B		Lot C		Lot D	
	A	C	A	C	A	C	A	C
Water soluble	22.5	22.4	22.4	22.2	21.8	21.5	22.8	22.9
Glucose	8.8	8.4	3.8	3.9	1.5	1.4	3.2	3.8
Tans/non tans	0.77	0.77	1.12	1.14	1.64	1.56	1.36	1.34
Total ash	0.31	0.30	1.07	1.08	1.18	1.25	0.37	0.35
Insol. ash	0.15	0.14	0.31	0.31	0.20	0.19	0.12	0.11
Epsom salts	0.12	0.12	1.80	1.90	1.07	1.10	0.44	0.40
Grease	1.8	1.8	2.8	3.00	2.7	3.0	2.0	2.0
Hide substance	37.8	37.4	35.5	35.6	34.4	34.6	36.3	36.5
Combined tan	25.7	26.2	27.0	26.9	29.0	28.7	26.9	26.5
Degree of tan	68	70	76	76	84	83	74	72

A= Average value representing average value for 15 bends. Determined from average of 20 samples each from different location on bends as shown in diagram on page 10, T. P. No. 138, Bureau of Standards. A sample for any particular location is a composite sample of all those locations in the 15 bends.

C= Calculated value from locations 11, 31 and 25 (Fig. 1, page 10, T. P. No. 138.) These locations were chosen as representing locations 3, 5 and 24 (samples for single bend analysis) diagram page 429, A. L. C. A. Committee Report, 1921, Sampling of Leather and its Preparatiou for Analysis.

[1] This JOUR., 16, 429 (1921).

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TABLE II.—CHEMICAL ANALYSIS OF STUFFED CHROME SOLE LEATHER ON BASIS OF MOISTURE CONTENT OF 12 PER CENT

	A	C
Water soluble	11.43	11.53
Hide substance	30.43	29.95
Grease	19.97	19.59
Cr_2O_3	2.86	2.84
Cr_2O_3 fat free	3.57	3.53
Glucose	4.88	4.78
Ash	20.42	20.46
$BaCl_2$ in water solubles	1.10	0.99

A= Average value for six bends from average of 26 samples from different locations on the bend. Each sample for a particular location is a composite sample of all the locations on the six bends.

C= Calculated value from locations 11, 31 and 26 representing locations 3, 5 and 24, A. L. C. A. Committee Report, page 429.

It is considered that the above comparisons afford a satisfactory confirmation of the work of the A. L. C. A. Committee.

With reference to the recommendation of the committee that it would be impracticable to specify locations from which cuttings should be made in terms of inches from the tail or from the edge, it is believed that for the purposes of specification work, this could readily be done and the representative sample assured. This would hold only if the units being purchased were uniform in size within certain limits. For example, it is believed that the following specification for location of the cuttings would be satisfactory when purchasing sole leather bends which do not vary in length more than 3 inches above or below an arbitrary standard of 56 inches, and in width more than 2 inches above or below an arbitrary standard of 28 inches.

> "The sample for chemical analysis of single sole leather bends shall consist of three cuttings each 8 inches x 2½ inches, located as follows: One cutting beginning at a point on the backbone edge 2 inches from the shoulder end, one cutting beginning at a point on the backbone edge 28 inches from the shoulder end, and one cutting beginning at a point on the belly edge 15 inches from the shoulder end. The 8 inch dimension shall run lengthwise of the bend."

The butt end could be used also as a reference point but in the case of bends it is considered more logical to use the shoulder end as a reference point since that end is squared from trimming the shoulder. The above is not given as a standard but simply

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serves as an indication of what might be done. If it is found that the unit being purchased consists of hides varying largely in size it would be more logical to express the location of the cuttings, from the reference point, in terms of percentages of the total length and width.

In the case of single bends of such leathers as belting and harness it appears from the data at hand that this method of sampling would not be representative of the tensile strength of the bend. The average value of the three cuttings is generally much higher than the average for the bend. This may be explained by the natural tendency of the shoulder and belly portions to have a greater tensile strength than the other portions. The indications are that the tensile strength of location 3, page 429, A. L. C. A. Committee Report, is fairly representative of the average for the bend. The table below gives the results of such a comparison made on six single harness leather bends.

TABLE III.—DATA ON TENSILE STRENGTH IN POUNDS PER SQUARE INCH FOR SIX SINGLE HARNESS LEATHER BENDS

Bend	A	C
A	3850	3580
B	4380	4060
C	4650	4680
D	4160	4340
E	4630	4850
F	4490	4495
Average	4360	4340

A = Determined from the average of 28 samples each from different locations on the bend.

C = Calculated value from location represented by location 3, diagram page 429, A. L. C. A. Committee Report.

BUREAU OF STANDARDS, WASHINGTON, D. C.

THE DETERMINATION OF WATER SOLUBLE IN LEATHER—PRELIMINARY COMMITTEE REPORT

G. W. Schultz, Chairman

The title of the determination—Water Soluble—naturally leads one to the belief that this determination should embrace all of the matter in leather which can be extracted from it by water and it has been toward this end that the past labors of individual and committee investigations have concentrated. These reports are fairly voluminous and contain much of interest concerning the nature of leather and its action toward water under different conditions of extraction, but it has been the writer's opinion that

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the point pursued was entirely different from the real object of the determination. What particular value has the result of a determination made by extracting a sample of leather with a relatively enormous volume of water at an arbitrarily high temperature? Do such results present a picture of the value of the leathers in service? It appears that they do not and therefore it was deemed desirable to have a definition for the term "Water Soluble" that would at least embrace one point, and the most desirable one, that such a determination should give. With this object in view an attempt was made to get the opinions of a number of chemists and tanners as to what information was most desired in a determination of water soluble in leather. The majority of those who had a decided opinion on the subject thought that the determination should give a measure of the load in leather. But this still leaves the term "load" to be defined.

It is well known that the results of a water soluble determination on sole leather is commonly viewed as the amount of material which may be washed out of the leather in the course of its service as a sole. The injustice in this respect of the present official method is adequately shown in Table I, wherein is given the data on five pairs of soles before and after wear which are typical results obtained in a test conducted by this laboratory in the fall of 1917. In Table IA is given the data on four different kinds of leather used in wear tests conducted by the Bureau of Standards which have been taken from *Technologic Paper*, No. 138.

In Table I it will be seen that although the epsom salt and sugars in the leather lose from about 60 per cent to 82 per cent of the total amount originally present, the loss in tanning material is seen to vary between 3.6 per cent as a minimum and 37.3 per cent, as a maximum, of the total amount found by the official method of extraction. These wear tests may be considered severe with regard to the action of water as they were conducted in the wettest season of the year. No information is given concerning the conditions under which the Bureau of Standard soles were worn but it can be seen from Table IA that the results are analogous to those given in Table I. A high percentage of the total amount of epsom salts and glucose is lost during wear but a relatively low per cent of the total amount of tanning material extracted by the official method is lost.

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TABLE I.

SHOWING LOSS OF EPSOM SALTS, SUGAR AND TANNING MATERIAL BY LEATHER IN THE COURSE OF SERVICE AS SOLES

NO.		Moisture	Hide substance	Epsom salts	Glucose	Water soluble	Tan. mat. in* water soluble
1	Before wear	13.00	26.32	2.48	3.68	21.17	15.78
	After wear	13.00	30.77	0.52	0.89	15.35	14.10
	Calc'd. to original basis		26.32	0.44	0.76	13.13	12.07
	Lostin wear			2.04	2.92	8.04	3.71
	Per cent of total lost			82.3	79.4		23.5
2	Before wear	13.00	23.77	2.44	4.59	22.14	15.81
	After wear	13.00	26.24	0.60	1.50	12.85	10.94
	Calc'd. to original basis		23.77	0.54	1.36	11.64	9.91
	Lost iu wear			1.90	3.23	10.50	5.90
	Per cent of total lost			77.9	70.4		37.3
3	Before wear	13.00	25.41	4.37	6.02	23.71	14.69
	After wear	13.00	26.88	1.68	2.33	13.76	10.27
	Calc'd. to original basis		25.41	1.59	2.20	13.01	9.72
	Lost in wear			2.78	3.82	10.70	4.97
	Per cent of total lost			63.6	63.5		33.8
4	Before wear	13.00	28.93	2.94	3.12	16.93	11.79
	After wear	13.00	39.13	1.22	1.76	17.98	15.38
	Calc'd. to original basis		28.93	0.90	1.30	13.29	11.37
	Lost in wear			2.04	1.82	3.64	.42
	Per cent of total lost			69.4	58.3		3.6
5	Before wear	13.00	31.17	3.68	3.64	20.74	14.57
	After wear	13.00	34.03	1.35	1.28	15.86	13.65
	Calc'd to original basis		31.17	1.24	1.17	14.53	12.51
	Lost in wear			2.44	2.47	6.21	2.06
	Per cent of total lost			66.3	67.9		14.1

* Water Soluble—[Glucose + (Epsom Salt × .6875)]: this factor for epsom salts was obtained as the average to which one part of epsom salts dried on the evaporator and dryer.

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TABLE IA.

SHOWING LOSS OF EPSOM SALTS, SUGAR AND TANNING MATERIAL BY LEATHER IN THE COURSE OF SERVICE AS SOLES

		Moisture	Hide substance	Epsom salts	Glucose	Water soluble	Tan. mat. in water soluble
	Before wear	12.00	36.8		9.6	23.4	13.8
Sample A;	After wear	12.00	41.9		0.5	13.6	
No. 15	Calculated to original		36.8		0.44	11.95	11.5
	Per cent of total lost				95.4		16.6
	Before wear	12.00	38.1		8.4	22.0	13.6
Sample A;	After wear	12.00	38.8		1.4	14.1	
average of 15 tests	Calculated to original		38.1		1.4	13.8	12.4
	Per cent of total lost				83.3		8.8
	Before wear	12.00	33.0	2.3	5.5	24.1	18.0
Sample B;	After wear	12.00	33.9	0.1	0.0	17.5	
No. 35	Calculated to original		33.0	0.1	0.0	17.0	16.9
	Per cent of total lost			95.7	100.0		6.0
	Before wear	12.00	36.2	1.7	3.7	22.1	17.2
Sample B;	After wear	12.00	35.5	0.7	1.1	19.7	
average of 15 tests	Calculated to original		36.2	0.7	1.1	20.1	18.5
	Per cent of total lost			59.0	70.3		
	Before wear	12.00	33.0		2.0	22.2	20.2
Sample C;	After wear	12.00	34.1		1.5	18.5	
No. 15	Calculated to original		33.0		1.45	17.9	16.45
	Per cent of total lost				27.5		18.6
	Before wear	12.00	35.4		1.4	20.9	19.5
Sample C;	After wear	12.00	34.8		1.3	20.9	
average of 15 tests	Calculated to original		35.4		1.3	21.3	20.0
	Per cent of total lost						
	Before wear	12.00	36.1		4.5	24.3	19.8
Sample D;	After wear	12.00	37.9		1.9	21.1	
No. 25	Calculated to total		36.1		1.8	20.1	18.3
	Per cent of total lost				60.0		7.6
	Before wear	12.00	36.8		3.1	22.4	19.3
Sample D;	After wear	12.00	36.8		1.8	21.2	
average of 15 tests	Calculated to original		36.8		1.8	21.2	19.4
	Per cent of total lost				40.7		

NOTE:—An extreme case and the average were taken from each kind of leather.

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It is the writer's opinion that the processes involved in the formation of leather may be roughly divided into two distinct operations. The first is the combination of tannin with hide which proceeds until the electrical charge of the hide is neutralized. This combination is conceived as being very stable towards water, but still subject slightly to hydrolysis. The second process consists of the deposition of tannin on, or the adsorption by, the hide-tannin combination which may proceed from stray or secondary valencies or other recognized hypothetical causes for this phenomenon. This secondary combination of tannin is enhanced by at least two factors, namely, time and concentration of liquor. On this assumption it would appear self evident that this combination is less stable toward water and that there may be tannin in the leather-forming substance which shows a graded variation in the degree of resistance to hydrolysis. The degree of resistance may be increased by the position in the complex, dehydration, molecular rearrangement or any of the causes which tend toward irreversibility. Thus it is conceived possible to have actual leather forming substance or the essential constituent of a leather that may be classed as soluble in water because it can be extracted from leather under certain conditions of extraction. However, before subjecting to conditions which bring about hydrolysis, it is combined with and is an intimate part of the leather fiber and as such plays its part in giving a desirable feature to certain kinds of leather. Therefore it does not seem justifiable to class this tanning material with that which is derived from the liquor occluded by the leather upon the removal from the tanning vat or the unadsorbed portion of that which is added by drumming in extracts, dipping in strong liquors, etc. Neither is it justifiable to class it with such materials as glucose, salts, etc. A piece of leather is conceived to consist of two component parts—the actual leather-forming part and the material which is present as a filler. It is for these reasons that *the determination of the water soluble in leather should give a measure of the amount of material in a leather which is soluble in water and which is in no manner combined with the hide substance or leather.* Then such a determination will give a measure of the

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load in a leather which is soluble in water, as the load may be considered as that portion of a leather other than the actual leather substance.

Experimental

In order to ascertain the relation between the amount of actual uncombined material in leather and the amount shown by a determination according to the official method of extraction, a number of experiments were made. Leather was drummed in solutions of tanning material long enough to give a reasonable assurance that equilibrium obtained throughout the leather. After removal of the leather from the tanning liquor and draining, the amount of water was determined in the leather. The concentration of the liquor from which the leather was removed was also determined. From the amount of water which the leather contained at the time of its removal from the liquor, the amount of liquor occluded by the leather was computed; and from the concentration of the liquor from which the leather was removed, the amount of uncombined tanning material in the air dry sample was calculated. It will be seen that in this work it has been assumed that the concentration of the external solution and that absorbed by the leather is the same and that all of the water found in the leather is present as solvent for the uncombined material at the time of its removal from the tanning solution. When equilibrium is established between a tanning liquor and a thoroughly tanned piece of leather it is highly probable that the former assumption is valid. Any increase that might be in the internal solution would be present as material adsorbed at the leather-water interface and could only be there by virtue of an attraction of the leather and hence could be considered as combined. Any exception to the latter assumption would tend to lower the amount of material calculated as present, but it cannot be conceived to have a material effect on it unless water is also adsorbed strongly by the leather.

Leather No. 1. This sample was tanned in a bottle in the laboratory by rotating in the shaker. After the final strengthening of the liquor, the whole was rotated seven days before removal of the leather.

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Weight of wet leather = 416.9 grms.

Weight of air dry leather = 166.2 + 0.8 gr. (weight of solids drained from the leather in drying).

Then the water lost in bringing the leather to the air dry condition =

416.9 — 167.0 = 249.9 grms.

Moisture in air dry leather = 8.47 per cent.

Moisture in 166.2 grs. leather = 14.08 grs.

Total amount of water in the leather when removed from liquor = 263.98 grms.

The final liquor gave on analysis:—Total Solids—9.87 per cent; Soluble Solids—8.06 per cent; Insolubles—1.81 per cent. The concentration of the solution after correcting for insolubles would be 8.21 per cent.

Then for every 91.79 parts of water that were present in the wet leather there was 8.21 parts of soluble solids deposited in it on drying. Therefore, there should have been 23.612 grms. of soluble tanning material in the leather that was not combined with it in any manner. Deducting the 0.8 grm. of solids that drained from the leather on drying, the resulting figure in 166.2 grms. of the air dry leather would be equivalent to 13.73 per cent of water soluble matter.

The following samples were handled, and the calculations were made in the same manner.

Leather No. 2. Taken from the last tanning vat and drummed in pure water.

Leathers Nos. 3 and 4. Taken from the last tanning vat together with some of the liquor from this vat and drummed in it.

Leather No. 5. Samples taken from belly edge of leather in the last tanning vat and drummed in liquor taken from the same vat.

Leather No. 6. Same as No. 5 with the exception that cuttings were taken from the back edge of the leather.

Leather No. 7. Cuttings from finished leather drummed in solution of bisulphited quebracho.

The data for these seven experiments are tabulated in Table II together with the results of water extractions according to the official method and extractions of 30 gram samples at 25° C.

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TABLE II.

Leather Number	1	2	3	4	5	6	7
Analysis of air dry leather							
Moisture	8.47	8.52	12.54	9.17	15.70	12.92	17.05
Ins. ash	0.10	0.10	0.10	0.11	0.10	0.10	0.11
Grease	0.21	0.22	1.89	0.57	1.62	0.26	2.71
Hide substance	45.67	43.60	34.83	37.24	33.31	39.27	31.97
Tanning material	45.55	47.56	50.64	52.91	49.27	47.44	48.16
Water in leather as removed, per cent	63.1	62.4	61.1	60.2	54.5	43.8	49.98
Analysis of liquor from which leather was taken							
T. S.	8.21	2.20	10.8	10.55	7.98	7.98	14.85
Purity	40.0	48.8	63.1	61.0	50.0	50.0	74.7
Per cent water soluble, uncombined tan. mat. in air dry leather. Calculated	13.73	3.49	16.78	16.19	8.75	5.88	14.47
WATER EXTRACTION BY PERCOLATION							
30 grams to 2 liters at 50° C., time 3 hours							
Per cent extr'd	22.02	14.47	26.28	26.33	21.53	18.63	25.30
Excess over calc'd	8.29	10.98	9.50	10.14	12.78	12.75	10.93
Purity of ext.	50.1	71.6		67.5	65.7	67.8	77.1
30 grams to 1 liter at 25°C., time 1½ hours							
Per cent extr'd	16.78	9.72	19.28	20.06	13.52	10.48	17.84
Excess over calc'd	3.05	6.23	2.50	3.87	4.77	4.60	3.37
Purity of ext.	43.1	64.5		61.0	55.6	56.4	72.0
PER CENT IN EXCESS OVER CALCULATED							
By official extraction	60.4	314.6	56.6	62.6	146.1	216.8	75.5
By extraction at 25° C	22.2	178.5	14.9	23.9	54.5	78.2	23.2

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to one liter in 1½ hours. A close inspection of the data in this table will give many points of interest. It shows plainly that the percentage excess of material extracted by the official method over the amount calculated to be in the leather varies widely, between 56.6 per cent and 314.6 per cent, and apparently that this percentage excess is greater the less the amount of actual uncombined material is present and vice versa. The results of extraction at 25° C. give a percentage excess over the amount calculated which varies between 14.9 per cent and 178.5 per cent, but with the exception of the latter figure the variation in percentage excess between individual leathers is not so great as found in the extractions at 50° C.

It will be seen that the purity of the extract at 50° C. in every case is considerably in excess of that of the liquor from which the leather was removed. The purity of the extracts obtained at 25° C. with one exception is still slightly higher than that of the respective liquors from which the leathers were taken. In this connection, attention is called to the fact that the purities of the liquors and of the extracts given here are not strictly comparable but are sufficiently so to serve as a guide. Forty-seven grams of wet hide powder were used in the analysis of the liquors which were of official analytical strength while from 25 to 30 grams were used for the leather extracts at the concentrations as obtained. It was recognized that such conditions would not give results that are strictly comparable, therefore several tests were run in order to obtain some idea of the divergence. In order to avoid possible complications along the line of the reputed claim that non-tannins are converted into tannin in the course of concentration, the weaker liquors were not concentrated to equal the stronger ones, but the original liquors from which the leathers were taken were diluted so as to equal the concentrations of the leather extracts and then analyzed under similar conditions. When the liquor from which leather No. 7 was taken was diluted to the concentration in total solids of the leather extract obtained by extracting 30 grams of the leather at 50° C. to 2 liters, and then analyzed using the same amount of wet hide as originally used for the leather extract solution, the purity was 74.5. When the liquor from No. 5 was treated in the same manner a purity of 48.9 was obtained at the concentration of the leather extract

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for No. 5 by the official method. Thus it can be seen that the purity of the leather extracts as given should be considered as lower than reality when compared with analyses of the original liquors. It seems that this difference will be greatly influenced by the nature of the tanning material in question and by the actual ratio of tannin to non-tannin in the solution; and will be greater the lower the concentration of the leather extract analyzed. In general, the purity of the leather extract at either temperature exceeds that of the original liquor by a greater amount the less the amount of uncombined material there is present in the leather. This seems to be fully in accord with conclusions of past investigations on the subject that there is an increase in amount extracted with increase in volume of water. When operating with a given volume of water that portion which is required for solution of the uncombined material is diverted from acting on the combined material. Hence with a low water soluble there will be a larger amount of combined material removed and therefore an extract of proportionately greater purity will be obtained.

If the data for leathers Nos. 3 and 5 be compared the injustice of such a method as the official will be made apparent. These two leathers have the same amount of total tanning material on the dry basis although in the condition as analyzed No. 3 contained slightly more, and hence in 30 grams of the sample there was more tanning material in No. 3 than in No. 5 which was subjected to the action of the same amount of water. These leathers were widely different in character also, No. 3 was flexible and loose while No. 5 had all of the characteristics of a heavily tanned leather—was firm and solid. No. 3 contained 16.78 per cent of uncombined tanning material while No. 5 contained 8.75 per cent, a little over half as much, while an official extraction gave but little difference between the two—26.28 per cent and 21.53 per cent respectively. A comparison of leather No. 1 which may be likened to a light, tanned leather and No. 6 which is a heavily tanned leather shows similar facts. Although in this case No. 1 contained considerably less total tanning material than does No. 6 yet it contains over twice as much uncombined material and an extraction by the official method gives 22.02 per cent and 18.63 per cent respectively. The amounts ex-

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tracted are nearly the same while at 25° C. to 1½ liters the amounts extracted approach nearer the true relation.

The endeavor to formulate a procedure that will give absolutely true results for uncombined material in leather is beset with many difficulties and seems impossible of attainment in the light of our present knowledge, and it seems that the best we can hope for at present is to alleviate in some degree the injustice imposed by the present method. Both temperature and volume of water are important factors in determining the excess of material removed over the actually uncombined. The actual amount of uncombined material, of fastly bound material and of that which is bound and presents different degrees of resistance to hydrolysis are all important factors when temperature and volume of water are constant. The same leather extracted before and after allowing its moisture content to change will give different results when extracting under a given temperature with a given volume of water providing the volume is sufficiently great. Because in 30 grams of the leather having the lower moisture content there will be a greater amount of tanning material, both combined and uncombined presented to the action of the same amount of water.

Some investigation was made of a method to determine the uncombined matter by shaking a given amount of leather with water, but considerably more difficulties were encountered in this direction, some of which were difficulties in operation. Results of this line of investigation on some leathers used above are given in Table III. It will be seen from this table that it is necessary to know the amount of uncombined material present in order to determine the amount of water to be used. If a smaller amount of water than 250 cc. should have to be used for 30 grams of leather, as is the case with leathers Nos. 2 and 6 the difficulties of operation may prove insurmountable as it is barely possible to get sufficient solution for the necessary tests when using 250 cc. Some other difficulties in operating this method are due principally to the fact that the solutions obtained after shaking for one hour contained much leather in colloidal suspension. After squeezing the solution through a linen cloth it was very muddy in appearance and a large portion of the suspended matter passed through the filter paper giving a muddy filtrate

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TABLE III.

SHOWING RESULTS OF WATER EXTRACTION OF LEATHER BY SHAKING THIRTY GRAMS FOR ONE HOUR. ROOM TEMPERATURE VARIED FROM 20°–22° C.

	No. 1	No. 2	No. 3	No. 4	No. 6	No. 7
Uncombined material present. Calculated.	13.73	3.49	16.78	16.19	5.88	14.47
30 grams— 250 cc. water		6.06	14.64		6.96	
30 grams— 500 cc. water	13.72	7.24	16.39	16.20	8.01	14.45
30 grams—1000 cc. water			17.68			

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TABLE IV.

SHOWING HOW THE WATER SOLUBLE CONSTITUENTS OF A LEATHER ARE REMOVED IN AN EXTRACTION BY PERCOLATION AT 25° C.

		1st 200 cc.	2nd 200 cc.	3rd 200 cc.	4th 200 cc.	5th 200 cc.	Total for 1 liter	By official method	Uncombined matter[2] present
Leather No. 8									
Total solids	Per cent of leather	24.33	2.23	1.30	0.68	0.57	29.11	35.83	
	Per cent of total extracted	83.6	7.7	4.5	2.3	1.9	100.0		
Sugars	Per cent of leather	8.32	0.26	0.0			8.58	8.45	
	Per cent of total extracted	97.0	3.0				100.0		
Epsom salts	Per cent of leather	7.69	0.26	0.05			8.00	7.99	
	Per cent of total extracted	96.1	3.3	0.6			100.0		
Tanning[1] material	Per cent of leather	10.72	1.78	1.26	0.68	0.57	15.03	21.88	
	Per cent of total extracted	71.3	11.8	8.4	4.5	4.0	100.0		
Leather No. 4									
	Per cent of leather	15.97	1.97	1.13	0.80	0.63	20.50	26.33	16.19
	Per cent of total extracted	77.9	9.6	5.5	4.0	3.0	100.0		
Leather No. 2									
	Per cent of leather	6.73	1.47	0.97	0.70	0.62	10.49	14.47	3.49
	Per cent of total extracted	64.2	14.0	9.3	6.7	5.8	100.0		

[1] Tanning material in this case is taken as the difference between total solids and the sum of sugars plus epsom salts times the factor .6875.

[2] Determined as described in foregoing part of this paper.

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even after repeated returning to the filter. Although the filtrate could be gotten clear eventually if it were returned often enough so that the pores were plugged up sufficiently to hold the suspended matter, then the rate of filtration was so slow that it required too long a time to obtain the requisite amount of filtrate to carry out the usual determinations. Kaolin served well to give a clear filtrate, but here, also, the filtration was slowed up to the same amount for the same solutions. The difficulty of conducting such tests at a predetermined temperature is also apparent.

TABLE V.

SHOWING THE REMOVAL OF THE WATER SOLUBLE CONSTITUENTS OF LEATHER IN CONSECUTIVE 200 CC. PORTIONS EXPRESSED IN PER CENT OF THE AMOUNT REMOVED IN AN OFFICIAL EXTRACTION. DATA TAKEN FROM TABLE IV.

		1st 200 cc.	2nd 200 cc.	3rd 200 cc	4th 200 cc.	5th 200 cc.	Per cent by official method
Leather No. 8							
	Sugars	97.0	3.0				8.45
	Epsom salts	96.1	3.3	0.6			7.99
	Tanning material	49.0	8.1	5.8	3.1	2.6	21.88
Leather No. 4	Tanning material	60.6	7.5	4.3	3.0	2.4	26.33
Leather No. 2	Tanning material	46.5	10.0	6.7	4.8	4.3	14.47

In the light of our present knowledge of leather it seems that a determination to give the amount of actually uncombined material in a leather can only hope to give an approximation of such but nevertheless such a method will greatly lessen the injustice of the present official method. After mature consideration it seems possible that such a method may be formulated by making the limiting conditions such as would remove all of such materials as sugars and epsom salts, which we know do not combine with the hide or leather, from a leather containing what could be considered as the ordinary maximum amount that would be present in leather. An investigation along these lines led to the examination of a leather containing a large quantity of salts and sugars in order to see the extent to which such materials were removed in an extraction by percolation. Thirty grams of leather were loosely packed in a glass percolator which was immersed in a water bath at 25° C., 150 cc. of distilled water were added and allowed to stand for 10 minutes when the excess solution was drawn off in a 200 cc. volumetric flask. Successive 50 cc. portions of water were added and allowed to run through immedi-

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ately and this was continued until 5 consecutive 200 cc. portions of percolate were collected. Total time was about one and one-half hours. The consecutive 200 cc. solutions were analyzed for salts, sugars and total solids. The solution obtained by an official extraction was also analyzed for these constituents. The total amount of magnesium found in each case was calculated to epsom salts which is not strictly true as a portion may exist in the leather in other forms. The data for the average of several determinations on a leather of this type are given in Table IV under Leather No. 8. Leathers No. 2 and No. 4 which are the same as used in the previous work were subjected to a similar procedure and these results are also given in Table IV. The ease with which such materials as sugar and salts are removed from leather by percolation is very apparent. Around 97 per cent of the total is removed in the first 200 cc. of percolate at 25° C. Approximately 100 per cent is removed in the first 400 cc. Therefore, it seems that 500 cc. of percolate will be more than sufficient to remove all of the sugars and salts present and therefore all of the actually uncombined material in a heavily loaded leather.

In Table V the data presented in Table IV is calculated to per cent of the amount extracted by an official determination. The parallelism between the results for the first 200 cc. on leather No. 8 and the data presented in Table I is striking when one considers that the former was obtained on finely disintegrated leather under more or less ideal conditions for removing the soluble matter as it goes into solution.

Addendum

In the course of a discussion of the preceding work Mr. Reed suggested that the leather extracts might be analysed to better advantage by adding an aliquot of the solution of leather extract to a solution of tanning extract so that the mixture would give a solution of approximately analytical strength. Following this suggestion the leather designated above as No. 8 was extracted by percolation at 25° and 50° C. In each case the percolate was collected in successive 500 cc. fractions. A solution of tanning extract was prepared equivalent to 10 times analytical strength and was filtered at this concentration to eliminate

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any interference by insolubles. The first 500 cc. fraction of leather extract was added to 50 cc. of this solution of tanning extract and the whole made up to one liter. The remaining three fractions of leather extract were added to 100 cc. portions of the tanning extract and made up to a liter. A blank test was made on 100 cc. of the tanning extract to 1 liter. All solutions were analysed using 47 grams of wet hide powder. Then the composition of the leather extracts was calculated from the difference between their solutions and the blank. The results were as follows:

TABLE VI.

	1st 500 cc.	2nd 500 cc.	3rd 500 cc.	4th 500 cc.	Total for 2 liters
Extraction at 25° C.					
Total solids %	28.00	1.10	1.02	0.70	30.82
Non-tans %	19.75	0.31	0.09	0.04	20.19
Purity	[1]29.5	71.9	91.1	94.3	
Extraction at 50° C.					
Total solids %	32.32	1.53	1.01	0.72	35.58
Non-tans %	19.80	0.27	0.15	0.07	20.29
Purity	[2]38.7	82.4	85.1	90.3	

[1] Purity after deducting sugar and salts = 58.7.
[2] Purity after deducting sugar and salts = 68.1.

It is interesting to note that the total amount of non-tans extracted at 25° and 50° C. are practically identical although the extraction with water at 50° C. removes about 4.7 per cent more total solids than at 25° C. It is also evident that nearly the whole of this difference is found in the first 500 cc. portion. The third and fourth 500 cc. fractions show the same amount extracted at both temperatures which seems to be practically all tannin.

The same procedure was applied to four other leathers and the time the leathers were in the tan liquors increases in the order in which they are numbered, that is, No. 9 was in the liquors for the shortest time and No. 12 for the longest time. The results obtained with these four leathers are given in Tables VII and VIII and it will be noted that they are, in general, the same as obtained with leather No. 8. The difference in the amount extracted between water at 50° C. and water at 25° C. is practically all tannin. That which is extracted by the second liter of water either at 50° or 25° C. is practically all tannin.

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TABLE VII.

SHOWING TOTAL SOLIDS AND NON-TANNINS IN THE WATER EXTRACTS FROM LEATHERS NOS. 9, 10, 11, 12.

Leather No.	Extraction at 25° C. 1st. liter T. S.	N. T.	2nd. liter T. S.	N. T.	Total T. S.	N. T.	Extraction at 50° C. 1st. liter T. S.	N. T.	2nd. liter T. S.	N. T.	Total T. S.	N. T.	Excess of total at 50° C. over total at 25° C. T. S.	N. T.
9	12.65	4.51	2.28	0.11	14.93	4.62	15.33	4.80	2.79	0.00	18.12	4.80	3.19	0.18
10	13.16	4.56	2.08	0.00	15.24	4.56	15.17	4.91	3.32	0.21	18.49	5.12	3.25	0.56
11	13.04	4.43	2.63	0.21	15.67	4.64	17.43	5.04	2.97	0.00	20.40	5.04	4.73	0.40
12	13.61	4.49	2.87	0.20	16.48	4.69	18.39	5.01	3.29	0.14	21.68	5.15	5.20	0.46

TABLE VIII.

SHOWING PURITY OF LEATHER EXTRACTS IN COMPARISON WITH THAT OF THE LIQUOR FROM WHICH THE LEATHER WAS TAKEN.

Leather No.	Liquor from which leather was taken Purity	Extraction at 25° C. 1st. liter Purity	2nd. liter Purity	Extraction at 50° C. 1st. liter Purity	2nd. liter Purity
9	43.6	64.4	95.2	68.8	100.0
10	52.4	65.3	100.0	67.6	93.7
11	65.7	66.0	92.0	71.1	100.0
12	66.8	69.2	93.0	72.7	95.8

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SUMMARY

It is claimed that the present official method for the determination of water soluble in leather gives results which have no definite meaning. If the determination is to include all matter which can be extracted from leather by water, then under its present limitations it falls far short of this purpose. It is shown in actual wear tests of sole leather that most of the salts and glucose are washed out but only a comparatively small fraction of the amount of tanning material which is designated as water soluble by the official method is lost under the conditions of wear. It is shown that the amount of tanning material which is extracted under the conditions of the official method is greatly in excess of that which is present in the leather through the occlusion of tanning liquor. It is also shown that the excess of tanning material extracted from leather with water at 50° C. over that extracted at 25° C. is largely, if not entirely, tannin and that the same is true for the material extracted at either temperature after the first liter of extract is obtained.

It is affirmed that water soluble in leather should be defined as that portion of the leather which is soluble in water and which is in no way combined with the hide or leather fiber, and that the determination should give a measure of such as nearly as is practical. It appears that the percolation method using a temperature of 25° C. and not more than 1 liter of water would be a step in this direction.

COMMENTS OF COMMITTEE MEMBERS

L. R. LEINBACH: I agree with your opinion that the determination of the water soluble in leather should give a measure of the amount of material in a leather which is soluble in water and which is in no manner combined with the hide substance or leather. I also believe personally that secondary valence is a factor to be considered and that possibly some tannin combined in this way is split off by too drastic extraction. In the light of our present knowledge it seems almost a hopeless task to eludicate definitely the nature of auxiliary valence as affecting the hide-tannin complex, but at the same time that point seems to me to be the crux of the whole situation.

Lacking this fundamental knowledge, it appears to me that the present method of extraction gives results which are decidedly

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valuable from a comparative standpoint, especially considering that some soles actually show an increase in water soluble content after being worn in a dry climate. With regard to the question of washing out salts and tannin, I think it is a case largely of solubilities, the solubilities of epsom salts and of glucose being greater than those of tannin and non-tans.

I think that researches into the fundamentals underlying the determination of water soluble in leather can best be undertaken by a single investigator or by a group of investigators devoting practically their entire time to this problem and attacking it probably by purely scientific means and from a scientific view-point.

H. C. REED: Relative to this question I wish to say that I am heartily in accord with the Chairman in the work that he has done thus far. This may be looked upon in a measure as pioneer work in that its evident purpose is to destroy the conception rather firmly planted in the mind of the leather chemist that the water solubles of leather are all those matters present in a leather which can be removed by water under conditions created with the purpose in view of removing the maximum. The conception of what constitutes the water soluble of leather as indicated in the report of the Chairman of the Committee is that "Water Soluble should be a measure of the amount of material in leather which is soluble in water and which is in no manner combined with the hide substance or leather."

The writer is in hearty accord with this conception and believes that the work already done and included in the report of the Chairman points to the correctness of the view-point. It is certain that no commercial wear to which sole leather is subjected will effect a removal of an amount of material that our present official method for water soluble determination indicates. Furthermore, it would seem that certain conclusions that have been drawn in the past in the work done upon water soluble determination have been in error, largely in judging from the results of tannin determinations on water solubles that inasmuch as there still remained in these water solubles certain proportions of non-tannin constitutents, true water solubles yet remained in the leather. Now it would seem that the non-tannins shown were not really present but came from the error introduced by analysis of dilu-

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tions so weak. What we are actually removing after a certain limited extraction with water is combined tannin, and it would seem entirely probable that hydrolysis will continue to remove combined tannin.

Hence it would seem that the present official method for water soluble determination is grossly unjust and yet the writer fully realizes the difficulty in formulating a method for the removal only of material that is actually uncombined. On the other hand no matter how great the difficulty every effort should be directed towards perfecting such a method.

The writer, some months back, suggested that in estimating the proportion of tannin present in the water soluble of leather, that weak solutions of water solubles should be brought to official strength by the addition of an extract, susceptible of easy duplication in analysis, in order that the error occurring from the analysis of weak dilutions be counteracted. He understands that such a method has proved of value; that practically all leathers extracted with 500 cc. of water at 25° C. showed absence of nontan upon further extraction. From this it would appear that 500 cc. of water at 25° C. will remove all legitimate water soluble since it has been further proved that the salts present are fully removed with 500 cc. of water under like conditions of extraction. But a point yet to be determined arises from the fact that the method of extraction cited will remove all the true water solubles from a heavily loaded leather, while in the case of an unloaded leather the extraction is too drastic, removing matters from leathers of the latter character that are not truly water solubles. In a previous letter to the Chairman the writer suggested the possibility of overcoming this difficulty by proportioning the amount of leather extracted to the probable water soluble content as predetermined by the results of the estimation of hide substance, water, grease and ash and he is still of the opinion that investigation along this line will prove of value.

C. C. Smoot, III and L. E. Stacy: If the term water solubles is to embrace all materials soluble in water, combined, adsorbed or uncombined by the hide fiber without any regard to its leather forming qualities the A. L. C. A. method is an effort in that direction; the extraction, however, not being complete. If we

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define leather to be a compound formed by establishing an equilibrium between hide and tannin, producing a definite hide tannin compound resistant to water, then all other solubles, soluble in water should be classed as water solubles. But it is hard for one in the sole leather game to conceive of sole leather as the hide with the electrical charge neutralized by mineral or vegetable tanning material and the presence of additional tanning materials not enhancing its wearing qualities. The attitude of the commercial world, the results of wearing tests, and the analysis on worn soles, all tend to back up this position.

After the hide tannin combination has been formed it is reasonable to assume that at the interface every ion of unlike sign tends to neutralize charges on the already formed leather compound; by additional adsorption, building around and strengthening the hide fibers. It is obvious that the longer this process goes on the more heavily tanned will the resulting leather be. As an illustration of this point we know of a piece of leather which had been tanned in layers for 120 days the last layer being a liquor of over 10 per cent tannin content. A piece of this leather was then left in the same solution for four years. An analysis showed a gain in tanning efficiency from 85 to 120 due almost entirely to the greater combination having taken place or the greater adsorption of tanning material by the hide fiber.

According to Schultz's law the ion with a higher valence will be adsorbed more strongly than the ion with the lower valence. It is reasonable to assume that the vegetable tannins vary in valence, therefore, some are adsorbed more strongly than others and form a higher degree of resistance to hydrolysis.

In commenting on the results obtained from our work in connection with the committee on water solubles in 1919, we made the following suggestions to the Chairman: "That additional work be done using lower temperatures and limiting the amount of solution used to at least 1,000 cc." These conclusions were arrived at based on the results shown in the following curve based on extractions made at 50° C. using the official method at that time. An inspection of the curve will show that after 800 cc. the curve approaches a straight line and the work done by

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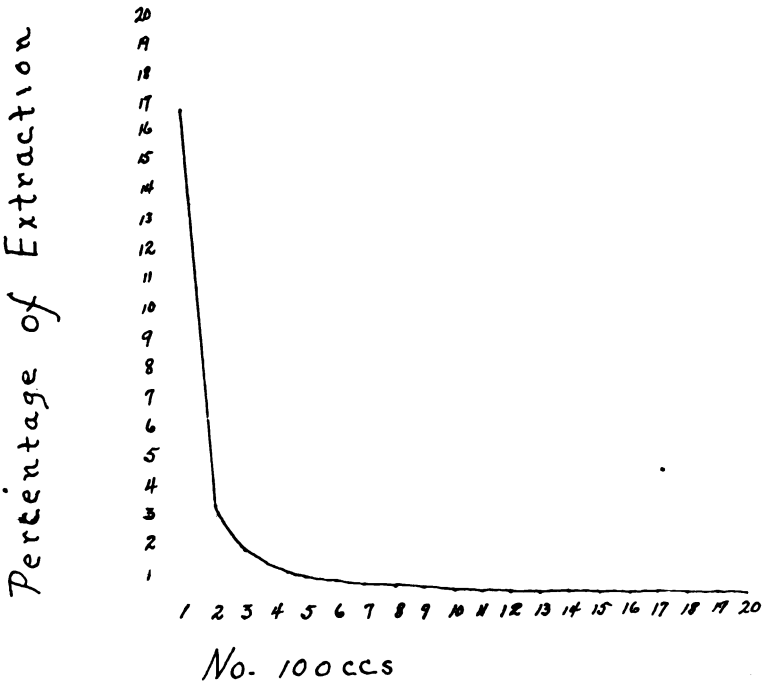
the Chairman shows that practically all of the material extracted beyond this point is tannin, which clearly shows hydrolysis.

We, therefore, believe that in view of the above that the Chairman's definition of water solubles offers a working basis; from which a method of real commercial value can be evolved.



S. K. JOHNSON: The present method of determining the water soluble material in leather not only dissolves out all of the soluble material added, but also some of the material which is necessary to properly tan hide substance. For instance when analyzing finished belt or harness leather, the present method shows a percentage of water soluble, which is dissolved some way from the hide itself. The washing this class of leather received during its manufacture should remove all the strictly water soluble material. Consequently, an analysis on a finished belt or harness leather should show no water soluble material, pro-

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vided none were added after scouring same. The more practical method of determining water soluble than the one in use at present would be one which would give a scouring shrink direct. For instance if rough leather is scoured and shows a shrinkage of 10 per cent in weight before it is greased and finished, then a method which would approximately show this shrink would be more advantageous from a tanners standpoint.

The term "Water Soluble Material" should mean those materials, excess tannin, sugar, salts, etc., which are easily soluble in water. It should not include any material which is not easily washed out under actual working conditions.

ABSTRACTS

South Indian Wattles. By K. C. Srinivasan. *Lea. Tr. Rev.*, **55**, 178 (1922). Analyses of samples of air dry bark from full grown trees indicate that the South Indian wattles compare very favorably with those of other countries.

	Tans	Non-tans
S. India (Nilghiris)	39.3 to 42.1	7.3 to 10.3
S. Indian (High Ranges)	40.1 to 44.1	7.1 to 13.0
Natal	35.2 to 39.8	7.3 to 10.3
Cape	40.1 to 44.1	7.1 to 13.0
East Africa II.	36.7 to 42.1	9.4 to 12.7
Australia	38.3 to 49.5	4.4 to 9.4
South Australia	40.2 to 46.5	9.0 to 9.4

The tannin from South Indian wattle barks is easily extracted and has no tendency to form phlobaphenes. Experiments with 5 year old bark from the High Ranges indicates that the optimum temperature for extraction is in the neighborhood of 60° C. when the most tannin is extracted and the proportion of non-tans to tannin is about the smallest. An investigation of the variation of tannin content with age of bark taken from the branches of trees in the High Ranges gave the following results:—

Age	1 Year	2 Years	3 Years	4 Years	5 Years
Tannins	18.37	24.37	25.97	27.62	29.07
Non-tannins	27.20	15.20	14.72	11.71	8.01
Insolubles	55.83	51.53	49.91	52.90	54.89
Moisture	8.60	8.90	9.40	7.77	8.03

Tanning trials with calf skin gave a full soft leather which when dried in the shade had a soft reddish tinge and on exposure to light darkened visibly. The feel of the leather was very good and it betrayed no tendency to crack. The penetration of the tannin was nearly as quick as of the Turved bark.

Laboratory experiments on the spent bark showed the possibility of at least producing a very satisfactory wrapping paper of excellent quality

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from the pulp. The wood of the wattle is said to yield 50 per cent of pulp capable of being used for the manufacture of strawboard. It is suggested that the destructive distillation of the wood will prove the most profitable.

Catechu-Tannins. I. Paullinia Tannin. By M. Nierenstein. *Trans. Chem. Soc.*, **121**, 23 (1922); through *J. S. C. I.*, **41**, 184A (1922). The tannin from *Paullinia cupana* seeds is shown to be a crystalline normal glucoside consisting of 1 mol. of dextrose and 2 mols. of gambier-catechin-carboxylic acid forming a depside. This gambier-catechin is not identical, but probably isomeric, with a previously described synthetic gambier-catechin (Annalen, 1913, **369**, 194). The formula, $C_{15}H_8O(OH)_5CO.O.(O.C_6H_{11}O_5)C_{15}H_8O(OH)_3COOH$, is assigned to paullinia tannin. By hydrolysis of its methylo-derivative it is shown that the catechol nucleus in 1 mol. of β-gambier-catechincarboxylic acid is combined directly with the other mol. of β-gambier catechincarboxylic acid and also with dextrose. Paullinia tannin, m. p. (dihydrate) 199°-201° C., (anhydrous) 259°-261° C. with decomposition, gives all the colour reactions of the catechu-tannins and forms crystalline alkali salts. Optical and other properties are described.

Occurrence of a Crystalline Tannin in the Leaves of *Acer Ginnala*. By A. G. Perkin and Y. Uyeda. *Trans. Chem. Soc.* **121**, 66 (1922) through *J. S. C. I.*, **41**, 184 A (1922). The leaves of *Acer ginnala* yield about 60 per cent of a crystalline tannin, acertannin, $C_{20}H_{20}O_{13}$, and 40 per cent or an amorphous mixture consisting of ellagic acid, quercetin, an amorphous tannin, mainly galloyl-aceritols, together with small amounts of a flavonol glucoside, and a substance probably a phlobo (catechol)tannin. Acertannin, crystallizes in two forms with 2 and 4 mols. H_2O respectively, and forms a crystalline octa-acetyl compound. It is hydrolyzed by 5 per cent sulphuric acid to 2 mols. of gallic acid and a dextro-rotatory sugar aceritol, $C_7H_{12}O_5$, m. p. 142°-143° C. Thus there are present two galloyl nuclei which are separately attached to the sugar nucleus. The resistance of acertannin to acids—of the order of gallotannin—indicates that it is a sugar ester and not a glucosido-gallic acid. Acertannin is unsuitable for tanning purposes, the hide being converted into a hard brittle material. It is, however, very suitable for the black dyeing of silk and cotton on an iron mordant. Aceritol behaves as a polyhydric alcohol, and is probably an anhydro-hexitol derived from mannitol or sorbitol.

Application of Fish Oils and Blubber Oils in Leather Making. By F. Maruyama. *J. Chem. Ind.* (Japan), **24**, 373 (1921). [*C. A.*, **16**, 853 (1921)]. A detailed review is given of the manufacture of chamois, buck, buff, helvetia, crown and Japanese white leather. In Japanese white leather manufacture, cowhide is tanned with rape-seed oil and sodium chloride. Certain improvements such as the use of fish and blubber oils are suggested.

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The Lignin-like Resins and Tannins of Spruce Needles. By A. C. von Euler. *Cellulosechem.*, 2. 128 (1921) and 3, 1 (1922); through *J. S. C. I.* 41, 171A (1922). Extracts obtained by treating spruce needles with 93 per cent methyl alcohol were divided into three fractions: "crude fat" soluble in ether; "crude resin" insoluble in ether but soluble in alcohol, and "molasses," a syrupy aqueous extract. From the "molasses" a whole series of definite tannic acids were isolated, all closely related in constitution, but differentiated by their solubilities in ether and in ethyl acetate and by their lead salts, some of which were colourless and some lemon-yellow. These tannins are ketonic acids derived from hydroxy-cinnamic acid and are closely related to *p*-cumarylferulic acid or feruylferulic acid and to caffeic acid; they occur in various stages of hydrogenation and hydration and represent hydroaromatic and hydrated derivatives of Klason's β-lignin. The constituents of the "crude resin" composing 10 per cent of the original needles are similar ketonic compounds of aldehydic and alcoholic function derived from the hydroxycinnamic aldehydes and alcohols; they also are tannins, and the alcoholic solution of the crude resin (which is not a true resin) precipitates gelatin. These substances are typical of Klason's α-lignin in various stages of hydrogenation and hydration. The crude resin is extremely susceptible to change, either spontaneously or on solution in alkali and re-precipitation by acid. A reddish-brown product called "tannin-red" is thus produced, which is analogous to the phlobaphenes from bark-tannins. The "crude fat" contains principally true fats and resins, but a similar tannin-like substance is present to the extent of about 29 per cent. This tannin is called abiephyllic acid, but this, as well as its closely allied derivatives, also appears to be built up from hydroxycinnamic aldehydes. The constitutional relationships of all these tannin-like substances to lignin is discussed, the structural analogies being very close, and the points of difference consisting in different degrees of hydrogenation, hydroxylation, methoxylation, and condensation.

Biology in Its Relationship to the Leather Industry. By F. A. Mason. *Leather Trades' Year Book*, 1921; *Le Cuir*, 10, 526 [*C. A.*, 16, 851 (1922)]. The importance of biological work in the leather industry is emphasized. The health of the animal, menaced by bacteria and parasites, affects the skin. The microscope has elucidated skin structure and liming can be microscopically controlled. Mites and worms, bacteria, enzymes, and molds entering into the various processes, usually with harmful results, are briefly described.

The Extraction and Leaching of Non-fibrous Tanning Materials. By J. A. Reavell. *Leather Trades' Year Book*, 1921; *Le Cuir* 11, 11 [*C. A.*, 16, 852 (1922). East Indian tanning materials are largely non-fibrous and yield much dust on grinding. A recent method of leaching consists in grinding the roughly ground bark to a fine dust under water and passing it through a series of leaches by means of compressed air or inert gas. A countercurrent of water is employed, and the dust retained from the final ex-

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tract by a sieve surrounding the interior of the leach. Stronger and clearer liquors are thus obtained, and the dangers attending the presence of fine impalpable dust are avoided.

Cause of Ripping of Outsoles. ANON. *Hide and Lea.*, Feb. 25, 1922. Two pairs of shoes of different manufacture, with the lock-stitch thread rotted out, were examined to determine the cause of such rotting.

An analysis for acidity in the sole leather and welt gave these results:

	Sole Per cent	Welt Per cent
No. 1	2.15	1.42
No. 2	1.07	0.17

To obtain the effect of acid, linen and cotton threads of equal size were treated with varying percentages of sulfuric acid. Five pieces of the same thread were used for each test; a portion of each thread was immersed for 10 seconds in the acid solution. The threads were then allowed to dry, at room temperature 75°, and the strength obtained on a Scott Tester, 8 inches between jaws, speed 20 inches per minute. The average of strength was taken from five threads and the averages of several of these tests taken at different times are given below:

	Per cent	Per cent	Per cent	Per cent
Per cent of sulfuric acid....None	.25	1	1.50	1.75
Average breaking strength 68.7	51	31.4	29	25

To show that the acid in the soles was responsible for the weakening of the thread, samples of thread were drawn through the middle sole taken from sample No. 1, after the sole had been wet, the thread was air dried for two days, then heated one hour at 214° F. and tested.

Original strength	After contact with sole	Per cent of loss
69	57	16

Pieces of thread measuring approximately three-eighth inch were removed from the outer sole of shoe No. 2 and the strength taken, although the results were variable, due to difficulty of manipulation, the strength of the thread was approximately half that of a normal thread.

Sulfuric Acid: Its Effect when Present to Excess in Leather. ANON. *Hide and Lea.*, Apr. 1, 1922. Sulfuric acid has its uses in the manufacture of sole leather, but it can be too freely used, with resultant and certain damage. Sulphuric acid should not be used in the dry dip or oil wheel. In the bleach only a sufficient amount should be used to offset the soda, the excess of same being carefully controlled. Instead of filler and acid, the use of carefully manufactured extracts of light color, with a fairly heavy non-tan content, are to be recommended. Care in selection and proper use of vegetable extracts will eliminate the necessity of sulphuric acid in the final stages of the manufacture of sole leather, with resultant benefit to the tanner, shoe manufacturer and public in general.

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Tannages of East Indian Sheep and Goat. By P. Smith. *Lea. Trades' Rev.*, **55**, 187 (1922). Of the various East Indian tannages those going under the trade names of C. D. C., Pitty and N. B. are the palest and best. For the spread of skin and clearness of tannage they cannot be compared. The C. D. C. tannage is a prime one, the only common defects being those caused by the "tick."

The good-grained clear skins make very good plain colours which are known in the trade as "smooths." They are generally used for bookbinding, and when made up equal calf, in fact it would be hard for anyone outside the trade to tell the difference. Those skins damaged by either "tick" or "blast" are also used for bookbinding, only they must be used for "purples," when their defects are covered by good dyeing.

Bookbinding skins must have a nice fine grain, and skins for this purpose must not be more than five-sixth pound in the crust. The heavier skins can be used up for purse, wallet, or bag work. To ensure a nice flesh it is advisable to have the skins buffed or shaved after being sorted for their respective purposes. It is absolutely essential for the uses mentioned, that the skin should possess a nice even colour, and to ensure this it is advisable to have them degreased.

The next in descending order are known as the City Tannages, which are known by their respective sources, Trichinopoly and Madras being the most important. These skins are distinguished by their nice pale colour, and are usually very spready, good pattern skins, which show they were selected pelts.

It is surprising to note in some of these class tannages the remarkable spread one may get for weight. It is also interesting to observe the flesh side of the skins, and to see how well they have been flayed; any of the city tannages make good velvets. Although these skins look remarkably free from grease they are heavily laden with sesame oil (up to 30 per cent of their weight), consequently they lose from one to two pounds per dozen when degreased. It is very seldom that bad flaying is noticed in this variety, and the flesh sides are usually free from defects. The grain, however, is very poor, being more or less spoilt by stains, blast, etc. A large proportion of these skins were once used for bookbinding, but they have declined in favour. Motor clothing is now made out of East Indian sheep.

The next to mention are Coimbatoires, which are similar to City Tannages, being a clean tannage, but the spread of the skin cannot be compared with the latter. The up-country tannages which come next are much darker in colour, being heavily laden with natural grease. Texture also is poor, the flesh is long, and they look as if they have been hardly dressed on the flesh side. These classes lose from 2 to 3 pounds when degreased. Bangalores, Bombays, Hyderabads are good examples of this class, the skins are soft and spongy, which shows that their treatment in the wet is much more primitive than with the city tannages. Their safest use is for black work, or they may be degreased and japanned.

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The next, Dindigul tannages, are easy to distinguish on account of their peculiar yellowish colour. They are, however, a good class of pelt, and, generally speaking, rather stouter than city tannages. They often lose as much as 3 pounds when degreased. The next and last to mention are the Middle Town Tannages, important examples of which are Vellores, Rashan and Nizan. They are very numerous, and have each its own characteristics. Their chief use is for black work, common colour, but lighter ones are used for linings, and stouter ones for embossing work.

The Colloid Content of Vegetable Tanning Extract. By A. W. Thomas and S. B. Foster. *Ind.* and *Eng. Chem.*, **14**, 191 (1922). An attempt was made to determine the potential difference of the particles in various extracts against the aqueous phase, *i. e.*, the difference in potential of the negative electrical charge on the particles against the positive charges of the ions in the water immediately in contact with the particles. The method used was the U-tube electrophoresis technic as described by Burton [Physical properties of Colloid Solutions, Chapter VII (1916)]. Although there is some doubt as to the absolute correctness of the values obtained the order of increasing potential difference was found to be:—Gambier, oak bark, chestnut wood, hemlock bark (Wis.), sumac, larch bark, osage orange, quebracho. The order of decreasing conductivities was found to be:—Sumac, gambier, oak bark, larch bark, hemlock bark, chestnut wood, osage orange, quebracho. P. D. measurements of a quebracho extract at different concentrations show that the P. D. increases with decreasing concentration which means that the weaker solution is more astringent than the stronger. The results obtained with quebracho show that the addition of hydrochloric acid lowers the P. D. and that dialysis increases it. A part of the latter is accounted for by dilution.

To ascertain the action of vegetable tanning extracts toward electrolytes, solutions of extracts containing 4 grams solids per 100 cc. were treated with various electrolytes in different concentrations and the volumes of precipitated material were measured after centrifuging. It is stated that the interpretation of the effects of the several electrolytes is masked by the salting out and chemical precipitation of the molecularly dispersed substances present in addition to the colloidal tannins. It was expected that the order of sensitiveness to precipitation by mono-, di-, and trivalent cations would help to show the order of magnitude of the potential differences of the particles against the aqueous phase. The conduct of the extracts shows that there is a large amount of colloidal matter present and that it belongs to a type of dispersion with properties between the intermediate and hydrophilic dispersion. Seven graphs are given showing the effect of various electrolytes upon solutions of tanning extracts. G. W. S.

Further Studies of the Physical Characteristics of Gelatin Solutions. By C. E. Davis and E. T. Oakes. *J. A. C. S.*, **44**, 464 (1922). The density in grams per cc. of a gelatin solution of any concentration at any temperature is equal to the density of water at that temperature plus 0.00290

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multiplied by the percentage concentration of the gelatin by weight. The fact that gelatin solutions increase in viscosity with ageing of solution at 35° while at 40° the viscosity is constant indicated a method of locating the transition point— Sol form A $\rightleftharpoons$ Gel form B, rather accurately and it was found to be at a temperature of 38.03°. Because of the absence of age effects at 40° viscosity measurements of 1 per cent gelatin solutions were made over a range of p^H values from 1.7 to 12.3. The maxima coincide very closely with those obtained by Loeb but the minimum lies between p^H 7 and p^H 8 instead of at the iso-electric point of p^H 4.7.

The viscosities of gelatin solutions of various concentrations at 40° C. conform to Arrhenius' viscosity formula. G. W. S.

The Drying and Swelling of Gelatin. Preliminary Note. By S. E. Sheppard and F. A. Elliott. *J. A. C. S.*, **44**, 373 (1922). That sheet gelatin prepared from a dilute solution absorbs more water and swells more than that prepared from more concentrated solutions has been noted by a number of investigators. This has been attributed to the internal structure of the gelatin but the authors are searching for a more obvious cause. Gelatin jellies, of given definite geometrical shape and water content, might be supposed to dry in such a way that the shape would remain unchanged. Such shrinkage, and a swelling exactly reverse thereto, may be termed isometric. Isometric shrinkage of jellies can only be obtained by very slow drying under conditions such that the environment is only slightly unsaturated as to water. Examination of a leaf gelatin that has been dried on a net shows that the dilation in length and breadth on swelling is very small in comparison to the increase in thickness. The increase of thickness is greatest for gelatin taken from the intermesh (which has the smallest original thickness) and least for gelatin taken at the nodes of the net (which has the greatest original thickness). Initiation of an external framework appears sufficient to explain the unilateral swelling of a sheet of dried gelatin. Since capillary initiation or induction appeared to be of fundamental importance for the drying and swelling of gelatin, experiments were made with cubes, cylinders and spheres with various modifications of procedures. With cubes it is evident that drying is initiated at the corners which dry and harden first, at this stage the faces of the cube are curved outward. As drying proceeds the faces recede and the edges become somewhat incurved. In the case of cylinders and spheres, shrinkage on drying is not uniform but produces a wrinkled surface. The authors conclude that the "case hardening" effect is responsible for two important phenomena in the swelling and drying of gelatin jellies. The first is that the greatest shrinkage and subsequent swelling takes place perpendicular to the largest evaporating surface. The second is the apparent influence of the original concentration of the jelly on its swelling limit subsequent to drying. This is regarded as being due to the initial case-hardening which preserves an approximate "skin extension" corresponding to the original figure. If this is correct there appears no need to postulate an internal sub-microscopic but super-molecular structure of the gelatin. G. W. S.

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Description of a Method of Modern Liming. By L. Houben. *Le Cuir*, 11, 20–21 (1922). The gradual developments in liming include first the use of sodium sulphide. Unfortunately this compound upon solution gives reaction products, particularly caustic soda, which have such tremendous swelling action that it cannot generally be used alone. Mixed with lime however it is a much milder chemical. The addition of neutral salts, such as sodium or calcium chloride, to a lime-sulphide liquor is another development. These salts so reduce the causticity of the liming solutions that the latter can be used in decidedly greater concentration without injury to the leather. A third development depends upon the fact that the smooth grain of skins unhaired with an arsenic sulphide-lime liquor is due to the formation of a calcium collagen compound only. It is therefore necessary to prevent the production of a similar sodium compound which can be readily done by the addition of an acid. A fresh lime of about 10 cubic meters for 35 to 40 hides is made up of 45 kgs. of slaked lime, 15 kgs. of crystallized sodium sulphide and 10 liters of hydrochloric acid. For a strong lime 90 kgs. of lime are used. For the first 3 or 4 lots of 35 hides 30 kgs. of lime, 10 kgs. of sulphide and 6 liters of acid are added, after which half these quantities are used. These limes are renewed once a month. The last development consists in speeding up the penetration of a strong liming liquor without harmful effects. The best proportions for the liquor are 8 kgs. of lime, 2.5 kgs. of sulphide and 1.7 liters of acid per 100 kgs. of hide. The hides are drummed for one-half day in this bath with the addition of a little water; the drum is then filled with water and run for one-half hour after which the hides are left in a pure lime for 24 hours. R. W. F.

"Spueing" of Chrome Leather. By H. Giusiana. *Le Cuir*, 11, 80-2 (1922). Chemical and microscopical examination of the troublesome stains on chrome leather especially, and commonly referred to as spueing, show that they are due entirely to fatty acids which are solid at the ordinary temperature and which deposit on the surface of the leather in the same irregular manner in which they were absorbed. Furthermore this trouble is the result of liberation of fatty acids through the use of acids in scouring or surface degreasing.

To avoid these stains it is recommended that only the quantity of grease or oil necessary for the desired suppleness and softness be used avoiding an excess; that the stuffing mixture be free from all fatty acids which are solid at ordinary temperature; and that in scouring the leather before finishing use only a light benzol, a weak solution of ammonia or ammonium carbonate, and not mineral or organic acids. If only the necessary quantity of grease has been used the grain will require but a slight degreasing.

In making up the greasing mixture see that it is free from any constituents which congeal at 5° C. Two parts of a potash-olein soap to one of neatsfoot oil gives a good emulsion which when used on the basis of 3 per cent of the wet weight of the leather produces a satisfactorily

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oiled leather. In making up the fat or nourishing liquor use only pure rain or condensed water to avoid the formation of any calcium soaps. The sulfoleates are particularly good for greasing leathers of light colors which do not permit the use of soaps. Sometimes it is necessary to add a little egg yolk in such cases. R. W. F.

An Apparatus for Dyeing. By P. Huc. *Halle aux Cuirs*, Feb. 19, 1922, 43-6. A sketch and description are given of an apparatus recently patented by Louis Darmais for dyeing wool, cotton and the like. The apparatus consists essentially of a vat with 3 compartments, the middle one of which contains the dye solution and is equipped with a steam coil for regulating the temperature. The 2 outer compartments contain the material to be dyed. The dye solution is drawn out of the bottom of the middle compartment by a pump and forced in at the bottom of the outside compartments, passes up through the material to be dyed and into the middle compartment again by valves, thus completing the cycle and giving automatic circulation. After dyeing, the material is washed by closing the valves of the middle compartment, and forcing water up through the outer compartments which are fitted at the ends with outlets for the water. The material to be dyed is held in place by a screen. The apparatus is composed chiefly of heavy wood. It requires from 2 to 3½ horsepower and has a capacity of from 200 to 300 kgs. of wool. R. W. F.

Centrifugal Filtration of Tanning Extracts. By E. Depasse. *Le Cuir*, 11, 83-6 (1922). Experiments in purification and clarification of tanning extracts by centrifugal filtration have proved very successful. Many types of centrifuges however are not satisfactory being either too limited in capacity or too complex to permit ready removal of sludge or deposits. Apparatus of the Hignette type has been found practical since it combines simplicity of construction with large capacity. A diagram and explanation of the apparatus are given. Analyses of extracts prepared without and with decantation, and with decantation and decolorizing by blood show, upon comparison with extracts made from liquors after centrifuging, decidedly lower insolubles in favor of the last. R. W. F.

"Stripping" Vegetable Colors from Leather. By A. Rigot. *Le Cuir*, 11, 87-9 (1922). Correcting shades and changing colors of leather are often necessary. Drumming with alum was one of the first processes employed and depends upon the acid reaction of the solution to dissolve a certain quantity of the color lake formed. This method yields results only when the desired change in shade is slight and cannot be used when a number of skins of different colors are to be stripped for recoloring a certain shade.

Decolorizing methods of other industries are not generally applicable to leather. Bleaching compounds of chlorine destroy the color but have also an objectionable tanning action on the skins. Sulphites and hydrosulphites give only a temporary modification of the color.

Treating the colored skins with a solution of potassium permanganate and then with a bisulphite to remove the manganese dioxide followed by

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thorough rinsing gives excellent decolorization without apparent change otherwise in the skins. Using this method however it soon becomes evident that for red shades a great deal more coloring matter is required than normally, due to the sulphur dioxide which is retained even after numerous washings. A modification of the permanganate method using, instead of a bisulphite, hydrogen peroxide and alum gives excellent results, the alum giving a suitable acidity for the skins and for the action of the peroxide. Recoloring after this treatment does not involve the risks which are run when bisulphite has been used. This procedure also serves to completely remove the so-called blue spots or alum spots and helps in reducing the effects of yolk-stain. R. W. F.

The Action of Some Leather Tanned with Synthetic Tanning Materials toward Hot Water. By W. MOELLER. *Zeitsch für Led. und Gerb. Chem.*, 1, 100 (1921). In a previous work on Fahrion's Boiling Test [Abst., THIS JOUR., 17, 145 (1922).] the opinion was expressed that this test would serve as an indication of the extent to which leather was tanned providing the nitrogen in the extract was determined. This paper presents the results of such an investigation on leathers made with Neradol D and ND, Ordoval G and 2G and Ewol. The results which are given in the table below are claimed to indicate that synthetic tannins of this type are not true tannins and that therefore the water resistance of such leathers is low.

Leather tanned with	% moisture	Abs. dry leather used I	% HS in abs. dry leather II	Residue in 100 cc. filtrate grms.	HS in 100 cc. filtrate grms	HS removed percentage of I	HS removed percentage of II
Neradol D	19.9	0.801	71.46	a 0.3880	0.2241	27.98	39.15
				b 0.4085	0.1807	22.55	31.57
Neradol ND	20.9	0.791	70.28	a 0.4505	0.3127	39.53	56.25
				b 0.4515	0.2943	37.21	52.94
Ordoval G	20.3	0.797	74.98	a 0.3805	0.2866	35.96	47.96
				b 0.4145	0.2834	35.56	47.42
Ordoval 2G	20.5	0.795	76.47	a 0.3230	0.2452	30.84	40.33
				b 0.3360	0.2375	29.87	39.07
Ewol	18.5	0.815	68.12	a 0.5770	0.2604	31.95	46.90
				b 0.2810	0.1991	24.43	35.96

a filtered through folded filter; b through linen.

The investigation is being extended to leathers made with mixtures of vegetable and synthetic tannins. G. W. S.

Tanning Processes in Gelatin Tanning. By W. MOELLER. *Zeitsch. für Led. und Gerb. Chem.* 1, 80 (1921). That portion of gelatin which takes part in tannage with formaldehyde, quebracho-tannin and chrome-tannin corresponds in the majority of cases to the coagulation value of the gelatin used. That part of the gelatin which is not coagulable is found remaining in the tanning liquid. Tannic acid gives an apparent exception to the above, as a gelatin solution after being treated with solutions of varying strengths of tannic acid only showed very small quantities of soluble nitrogenous matter in the filtrate. This exception is explained by the sudden formation of membranes and the enclosure of untanned gelatin. G. W. S.

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Prescriptions and Recipes of the Tanner. By J. Jettmar. *Gerber*, **46**, 127 (1920); **47**, 140, 10 (1921). The instructions for taking off hides and skins issued in 1916 by the Interessenverband Deutscher Häuteverwertungen in Berlin are given and the recommendations of the Kriegsfell A.-G. in Leipzig for taking off rabbit, hare, and cat skins. The hide or skins are preserved either by dehydrating by drying or with hygroscopic salts, or they are sterilized. Drying of hides can be carried out in the air or special drying rooms and must be done as quickly as possible at a low temperature. They should not be dried in the sun or close to hot heaters as they will be excessively dried out. When dried at too high a temperature the interior of the hide may remain moist and putrify. In order to prevent putrefaction while drying a dilute solution of some antiseptic can be painted on the flesh, either carbolic acid, lysol, creolin (1 part in 500 of water) or sublimate (1 part in 2,000 of water). Formalin is not to be recommended since this spoils the glue stock and makes the hide fibers hard. Common salt is mostly used as a dehydrating material although calcined sodium sulfate, magnesium sulfate, soda and others can be used. The most suitable denaturant for salt is soda. Methods of salting hides and skins are described together with recommended methods for denaturing salt and patents for preserving hides. Dry salting is not to be recommended where wet salting is possible. The treatment of hides and skins with earth for the purpose of preservation is inadequate.

For the disinfection of anthrax infected hides the method of Schattenfroh and Kohnstein is given which is prescribed by the German Health Office for freshly removed hides from anthrax infected carcasses. The methods of the U. S. Bureau of Animal Industry and the Seymour-Jones method are also given. G. W. S.

PATENTS

Drying Leather. British Patent 172.200. W. Lee and R. Webber, both in Bedminster, Bristol. Nov. 2, 1920. A rack from which skins, etc., and particularly leather sheets during drying are suspended.

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Prompt co-operation of the chemists in the trade will result in a mutual benefit to those seeking employment and those desiring chemists.

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THE NINETEENTH ANNUAL MEETING
BIGWIN INN, CANADA
June 21st, 22nd, 23rd

The committee in charge presents as a tentative program the following addresses to be delivered at the Annual Convention of the Association:

Address by the President ..... F. H. Small.

The Mode of Occurrence of Tannin in the Living Cell ..... Professor F. E. Lloyd of the Department of Botany, McGill University, Montreal.

An address on The Swelling of Gelatin ..... C. R. Smith of the Bureau of Chemistry, Washington, D. C.

The Science of Curing.....Department of Leather Research, Cincinnati, Ohio.

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The Practice of Curing.....Department of Leather Research, Cincinnati, Ohio.

The Bacteriology of the Fresh Hide.....Department of Leather Research, Cincinnati, Ohio.

A Layman in Research ..... F. M. Moffat, Chairman of The Tanners' Research Committee.

The Influence of Atmospheric Humidity on the Strength and Stretch of Leather ..... The Bureau of Chemistry, Washington, D. C.

Preservation Effect of Oils and Greases on Leather ..... The Bureau of Chemistry, Washington, D. C.

Syntans and Mixtures of Syntans with Vegetable Tans.....S. Kohn.

Distribution of Grease in Leather.....L. Balderston.

Time Reduction in the Tanning Process ..... R. O. Phillips.

In addition to the special addresses to be delivered, Committee Reports will be given, and discussions will take place relative to the various problems confronting the industry.

Contributions of papers are expected from several prominent leather chemists of the Society of Leather Trades' Chemists. A very cordial letter has been received from the Secretary of that Society wishing our Conference every success and expressing the regret that Canada is too remote from England for them to send an official delegation to represent them at the meeting and further advising that we might expect papers from several of their members.

Specific information as to the details of the program, including entertainment activities, train schedules, railway rates, etc., will be sent to the members at a later date.

Attention is again called to the hotel rate extended to the membership by the Bigwin Inn management:

AMERICAN PLAN—$6.00 per day, per person, American funds.

The above rate quoted will be in effect from June 20th to July 15th. Reservations should be made by communicating direct with the management of the Bigwin Inn.

H. C. REED.
Chairman of Program Committee.

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COMPARATIVE ANALYSIS OF TANNING MATERIALS—1922 COMMITTEE REPORT

H. C. Reed, Chairman

The report of the Committee on Comparative Analysis for the years 1921 and 1922 is herewith submitted. The Chairman has not many comments to make on these results. He believes that the chief value of this collaborative work is to the analyst himself, in that it enables him to ascertain how closely he is in agreement with other analysts and general average.

At the same time the figures are interesting in disclosing wherein lies the chief weakness of the official method. In all, eighteen analysts participated in the work and the results of all are included and in the averages none of the results are omitted. It seems to the Chairman that the non-tannin determinations are, on the whole, in excellent agreement; far better, in fact, than is shown in the soluble solids determinations reflected in the insolubles item. It is rather strange however, that in the case of the hemlock bark extract really very excellent concordance is shown, as in this instance the insolubles were in very close agreement. The greatest lack of concordance appears in the soluble solids determination in the case of the Solid Ordinary Quebracho Extract and it would seem as though a committee should be appointed to investigate just why such wide variations occur in the analysis of this material in respect to the soluble solid filtration. It would seem as though concentrated effort should disclose why one analyst should find an insoluble content of 11.47 per cent and another analyst an insoluble content of 5.94 per cent in the self-same sample. As stated, no results were discharged in figuring averages although in a few instances the official method was not observed in the amount of dry hide for 200 cc. of solution.

An inspection of Tables IV and V will disclose that the wide differences obtained in some instances by the analysts was unquestionably due to differences in extraction.

All of the analysts used No. 1 F. Swedish filter paper for both soluble solids and non-tannin determinations with the exception of Messrs. R. W. Frey and L. R. Leinbach who used S. and S. No. 590, G. V. Downing who used the Alpha paper for the non-tannin determinations and R. E. Porter who used

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TABLE I.—SOLID ORDINARY QUEBRACHO EXTRACT DILUTION 5½ GRAMS PER LITRE.

Analyst	Moisture	Total solids	Soluble solids	Insoluables	Non-tannin	Tannin	Grams wet hide per 200 c c.	Per cent water in wet hide	Grams dry hide per 200 c c.	Appearance of filtrates Soluble solids	Non-tannin
L. E. Chamberlain	11.28	88.72	78.89	9.83	7.01	71.88	45.0	73.00	12.49	C	C
R. W. Frey and L. R. Leinbach	11.32	88.68	80.86	7.82	6.42	74.44	46.5	74.00	12.10	Sl O	Cl
C. A. Blair	10.45	89.55	80.94	8.61	5.98	74.96	48.0	72.40	13.25	Cl	Cl
G. V. Downing	8.17	91.83	80.36	11.47	6.59	73.77	46.5	73.00	12.56	Cl	Cl
V. J. Mlejnek	11.99	88.01	82.07	5.94	5.93	76.14	47.0	73.05	12.67	C	Cl
F. F. Marshall	11.45	88.55	80.55	8.00	6.01	74.54	46.5	73.05	12.53	Cl	Cl
T. S. Dunnigan	10.54	89.46	80.00	9.46	6.12	73.88	45.0	72.40	12.42	Cl	Cl
J. C. Dickson	12.07	87.93	79.68	8.25	5.82	73.86	47.0	72.60	12.88	Cl	Cl
L. E. Stacy	11.29	88.71	80.83	7.88	6.82	74.01	47.0	73.60	12.43	Sl O	Cl
C. R. Oberfell	11.47	88.53	78.81	9.72	5.69	73.12	46.5	72.60	12.74	Cl	Cl
R. E. Porter	11.35	88.65	79.50	9.15	6.57	72.93	46.5	73.80	12.18	Sl O	Cl
H. Anderson and R. Hart	10.61	89.39	80.61	8.78	6.60	74.01	47.0	73.50	12.46	Cl	Cl
T. A. Faust and L. G. Glass	8.02	91.98	82.72	9.26	6.83	75.89	47.0	72.50	12.93	Cl	Cl
J. E. McNutt	10.71	89.29	82.01	7.28	6.23	75.78	47.0	73.25	12.57	Cl	Cl
P. I. Neeld	11.60	88.40	81.07	7.33	6.16	74.91	46.5	72.50	12.79		
Average	10.82	89.18	80.59	8.59	6.32	74.27	46.6	73.15	12.60		
Greatest difference	4.05	4.05	3.91	5.53	1.32	4.26					
Greatest difference from average	2.80	2.80	2.13	2.88	.69	2.39					

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TABLE II.—CHESTNUT WOOD EXTRACT DILUTION 14 GRAMS PER LITRE.

Analyst	Water	Total solids	Soluble solids	Insoluables	Non tannin	Tannin	Grams wet hide per 200 cc.	Per cent water in wet hide	Grams dry hide per 200 cc.	Appearance of filtrates: Soluble solids	Appearance of filtrates: Non-tannin
L. E. Chamberlain	53.86	46.14	43.02	3.12	14.24	28.78	45.0	72.25	12.49	Cl	Cl
R. W. Frey and L. R. Leinbach	54.01	45.99	43.35	2.64	14.25	29.09	46.5	74.00	12.10	Cl	Sl O
C. A. Blair	53.74	46.26	43.78	2.48	14.35	29.43	48.0	72.40	13.25	Cl	Sl O and Co
G. V. Downing	53.41	46.59	43.81	2.78	13.75	30.06	46.5	73.00	12.56	Cl	Sl Co and O
V. J. Mlejnek	54.29	45.71	43.43	2.28	13.91	29.52	47.0	73.05	12.67	C	Sl O
F. F. Marshall	54.03	45.97	43.06	2.91	14.45	28.61	46.5	73.05	12.53	Cl	Sl O
T. S. Dunnigan	53.50	46.50	43.79	2.72	14.08	29.71	45.0	72.40	12.42	Cl	Cl
J. C. Dickson	54.50	45.50	42.74	2.76	13.56	29.18	47.0	72.60	12.88	Cl	Sl O
L. E. Stacy	53.85	46.15	43.25	2.90	14.59	28.66	47.0	73.60	12.43	Cl	Sl O
C. R. Oberfell	54.29	45.71	43.16	2.55	14.05	29.11	46.5	72.60	12.74	Cl	Sl C
R. E. Porter	53.85	46.15	43.80	2.35	13.85	29.95	46.5	74.00	12.09	Cl	Sl O
H. Anderson and R. Hart	53.98	46.02	43.64	2.38	14.27	29.37	47.0	73.50	12.46	Cl	Sl O
T. A. Faust and L. G. Glass	53.86	46.14	43.10	3.04	14.23	28.87	47.0	72.50	12.93	Cl	Cl
J. E. McNutt	53.98	46.02	43.58	2.44	13.96	29.62	47.0	73.25	12.57	Cl	Sl Co
P. I. Neeld	54.33	45.67	42.19	3.48	13.76	28.43	46.5	72.50	12.79	Cl	O
Average	53.97	46.03	43.31	2.72	14.09	29.22	46.6	72.97	12.60		
Greatest difference	1.09	1.09	1.62	1.20	1.03	1.63					
Greatest difference from average	.56	.56	1.12	.76	.53	.84					

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TABLE III.—HEMLOCK BARK EXTRACT DILUTION 16½ GRAMS PER LITRE.

Analyst	Water	Total solids	Soluble solids	Insoluables	Non-tannin	Tannin	Grams wet hide per 200 cc.	Per cent water in wet hide	Grams dry hide per 200 cc.	Appearance of filtrates: Soluble solids	Appearance of filtrates: Non-tannin
L. E. Chamberlain	57.93	42.07	38.19	3.88	12.33	25.86	45.0	72.25	12.49	Sl C	Sl Co
R. W. Frey and L. R. Leinbach	57.89	42.11	38.20	3.91	12.91	25.29	46.5	74.00	12.10	Cl and Sl O	Cl and Sl O
C. A. Blair	57.74	42.26	37.89	4.37	13.23	24.66	48.0	72.40	13.25	Cl	Sl Co
G. V. Downing	57.67	42.33	37.56	4.77	12.64	24.92	46.5	73.00	12.56	Cl	Sl Co
V. J. Mlejnek	58.06	41.94	37.87	4.07	12.59	25.28	47.0	73.05	12.67	C	Sl O
F. F. Marshall	58.02	41.98	37.46	4.52	12.88	24.58	46.5	73.05	12.53	Cl	O
T. S. Dunnigan	58.06	41.94	38.00	3.94	12.79	25.21	45.0	72.40	12.42	Cl	Cl
J. C. Dickson	57.99	42.01	37.69	4.32	12.37	25.32	47.0	72.60	12.88	Cl	Cl
L. E. Stacy	57.95	42.04	37.85	4.19	13.10	24.75	47.0	73.60	12.43	Cl	Sl O
C. R. Oberfell	58.07	41.93	37.03	4.90	12.80	24.23	46.5	72.60	12.74	Cl	Sl C
R. E. Porter	57.85	42.15	37.75	4.40	12.80	24.95	46.5	73.80	12.18	Sl O	Sl C
H. Anderson and R. Hart	57.76	42.24	37.87	4.37	13.07	24.80	47.0	73.50	12.46	Cl	Sl Co
T. A. Faust and L. G. Glass	57.78	42.22	37.70	4.52	12.82	24.88	47.0	72.50	12.93	Cl	Sl Co
J. E. McNutt	57.81	42.19	37.71	4.48	12.62	25.09	47.0	73.25	12.57	Cl	Cl
P. I. Neeld	58.27	41.73	37.37	4.36	12.63	24.74	46.5	72.50	12.79		
Average	57.87	42.13	37.74	4.39	12.77	24.97	46.6	72.97	12.60		
Greatest difference	.60	.60	1.17	1.02	.90	1.63					
Greatest difference from average	.40	.40	.71	.51	.46	.89					

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TABLE IV.—VALONEA BEARD—8 GRAMS PER LITER.

Analyst	Water	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	Tan dry basis	Grams wet hide per 200 c.c.	Per cent water in wet hide	Grams dry hide per 200 c.c.	Appearance of filtrates: Soluble solids	Appearance of filtrates: Non-tannin
L. E. Chamberlain	9.00	66.07	64.08	1.99	15.72	48.36	53.14	45.0	72.25	12.49	Cl	Cl
R. W. Frey and L. R. Leinbach	9.91	67.05	64.38	2.67	17.41	46.97	52.14	46.5	74.00	12.10	Cl	Cl
C. A. Blair	9.10	67.74	65.87	1.87	16.16	49.71	54.69	48.0	72.40	13.25	Cl	Sl Co
G. V. Downing	9.55	68.59	66.18	2.41	17.97	48.21	53.30	46.5	73.00	12.56	Cl	Sl Co
V. J. Mlejnek	10.12	66.93	65.05	1.88	15.49	49.56	55.08	47.0	73.05	12.67	Sl C	Sl C
F. F. Marshall	9.89	66.91	65.91	1.00	15.90	50.01	55.50	46.5	73.05	12.53	Cl	Cl
T. S. Dunnigan	9.40	70.00	68.75	1.25	17.40	51.35	56.68	45.0	72.40	12.42	Cl	Cl
J. C. Dickson	10.09	63.91	61.16	2.75	15.03	46.13	51.31	47.0	72.60	12.88	Cl	Cl
L. E. Stacy	9.46	66.09	65.21	.88	16.74	48.47	53.53	47.0	73.60	12.43	Cl	Cl
C. R. Oberfell	9.28	68.31	65.75	2.56	18.31	47.44	52.29	46.5	72.60	12.74	Cl	Cl
R. E. Porter	11.00	65.70	64.60	1.10	15.60	49.00	55.06	46.5	73.80	12.18	Cl	Sl O
H. Anderson and R. Hart	9.67	67.89	66.88	1.01	16.90	49.98	55.33	47.0	73.50	12.46	Cl	Cl
T. A. Faust and L. G. Glass	10.42	64.19	63.11	1.08	16.13	46.98	52.44	47.0	72.50	12.93	Cl	Cl
J. E. McNutt	9.35	68.13	66.58	1.55	15.54	51.04	56.30	47.0	73.25	12.57	Cl	Cl
P. I. Neeld	9.37	63.05	60.56	2.49	16.29	44.37	48.96	46.5	72.50	12.79		
Average	9.71	66.72	64.94	1.78	16.44	48.50	53.72	46.6	72.97	12.60		
Greatest difference	2.00	6.95	8.19	1.87	3.28	6.98	7.72					
Greatest difference from average	1.29	3.67	4.38	.97	1.87	4.13	4.76					

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TABLE V.—MANGROVE BARK—8 GRAMS PER LITRE

Analyst	Water	Total solids	Soluble solids	Insolubles	Non-tannin	Tannin	Tan dry basis	Grams wet hide per 200 cc.	Per cent water in wet hide	Grams dry hide in 200 cc.	Appearance of filtrates: Soluble solids	Appearance of filtrates: Non-tannin
L. E. Chamberlain	11.00	59.72	58.63	1.09	11.54	47.09	52.91	45.0	73.00	12.49	Cl	Sl Co
R. W. Frey and L. R. Leinbach	12.37	61.52	60.32	1.20	11.26	49.06	55.99	46.5	74.00	12.10	Cl	Cl
C. A. Blair	11.40	58.54	57.50	1.04	10.32	47.18	53.25	48.0	72.40	13.25	Cl	Sl Co
G. V. Downing	10.64	62.41	60.43	1.98	11.96	48.47	54.24	46.5	73.00	12.56	Cl	Sl Co
V. J. Mlejnek	12.36	60.89	59.64	1.25	10.99	48.65	55.51	47.0	73.05	12.67	Cl	Sl Co
F. F. Marshall	12.34	60.60	59.70	.90	10.58	49.12	56.03	46.5	73.05	12.53	Cl	Cl
T. S. Dunnigan	10.40	65.37	64.12	1.25	13.34	50.78	56.67	45.0	72.40	12.42	Cl	Cl
J. C. Dickson	12.18	61.89	61.10	.79	11.28	49.82	56.72	47.0	73.50	12.46	Cl	Cl
L. E. Stacy	11.45	62.88	62.13	.75	11.58	50.55	57.09	47.0	73.60	12.43	Cl	Cl
C. R. Oberfell	11.37	62.46	62.09	.37	11.94	50.15	56.59	46.5	72.60	12.74	Cl	Cl
R. E. Porter	11.45	59.95	59.20	.75	10.20	49.00	55.34	46.5	71.10	13.44	Cl	Sl O
H. Anderson and R. Hart	11.14	64.03	62.35	1.68	11.96	50.39	56.71	47.0	73.50	12.46	Cl	Sl Co
T. A. Faust and L. G. Glass	12.21	59.83	58.60	1.23	10.27	48.33	55.05	47.0	72.50	12.93	Cl	Sl Co
J. E. McNutt	12.00	61.49	59.85	1.64	11.86	47.99	54.66	47.0	73.25	12.57	Cl	Cl
P. I. Neeld	11.30	59.50	58.40	1.10	10.82	47.58	53.64	46.5	72.50	12.79		
Average	11.57	61.41	60.27	1.14	11.33	48.94	55.34	46.6	72.90	12.66		
Greatest difference	1.97	6.83	6.62	1.61	3.14	3.69	4.18					
Greatest difference from average	1.17	3.96	3.85	.84	2.01	1.85	2.43					

C—Cloudy; Cl—Clear; Co—Colored; O—Opalescent; Sl—Slightly.

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No. o Swedish for soluble solids and No. 588 S. and S. for non-tannins. The slow cooling method was used on all three extracts by all analysts. A number of analysts reported rapid cooling in the case of the mangrove bark and valonea beard.

In conclusion the Chairman would say that in the case of the non-tannin determinations concordant results are possible when the method is strictly adhered to but he believes that even strict adherence to the method will not invariably give concordant results in the case of the soluble solids determination on certain materials and it is for this reason that he has recommended that an investigation be made by a committee of the association to ascertain what may be the cause of these differences.

THE DETERMINATION OF MOISTURE IN LEATHER—1922 COMMITTEE REPORT

F. P. Veitch, Chairman

Although the manipulation is simple and the chances of error apparently small, there is no determination which the analyst has to make upon which collaborative work yields less satisfactory agreement than that of moisture in organic materials. An inspection of the records of collaborative work during the past thirty years shows that the problem has been considered from many angles, types and sizes of ovens have been considered, dryings have been made in air, in vacuum and in an atmosphere of inert gas at normal and reduced pressures, at temperatures varying from 60° (in vacuum) to 110° and from several hours to as long as 30 or more, and still there is no method by which two analysts working in different laboratories can be sure of securing agreeing results. Or shall we simplify the statement and say that no two analysts can get agreeing results on moisture in organic materials. On materials containing from 6 to12 per cent of moisture the results of collaborating analysts often vary from 1 to 3 per cent—1 per cent is usual. The results of four analysts reported by the Committee on the Determination of Moisture in Leather, 1920, of this Association, differed 0.69 per cent on a heavily greased harness leather containing about 6½ per cent of moisture and 1.4 per cent on a belting leather, after 16 hours drying.

Having these facts in mind, the Chairman has felt the hopelessness of accomplishing much in improving the concordance in

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TABLE I.—REPORT OF COLLABORATIVE A. L. C. A. WORK ON THE DETERMINATION OF MOISTURE IN LEATHER (1922).

Collaborator	Average R. H. when charges weighed per cent	Hours of drying in evaporator and dryer: 5	10	15	20	25	30	35	40	45	50	Average R. H. beginning and ending of drying per cent
		Per cent Moisture*										
L. Balderston												
Per cent R. H. beginning and ending of drying	55	10.22 55-51	10.40 53-46	10.44 62-54	10.65 48-43	10.79 41-39	10.73[1] 59-50	10.74 65-52	10.65[1] 78-69	10.50[1] 87-79	10.75 68-63	61-55
W. K. Alsop and L. A. Cuthbert												
Per cent R. H. beginning and ending of drying	43	9.67 43-43	9.87 43-43	10.15 37-35	10.19 33-39	10.31 43-41	10.42 43-41	10.41[1] 47-44	10.28[1] 42-48	10.31 45-42	10.67 42-35	42-41
Robert Wright												
Per cent R. H. beginning and ending of drying	64	9.09 64-64	9.31 63-62	9.57 66-65	9.48[1] 76-70	9.65 66-59	9.87 56-54	9.98 61-59	10.01 62-60	9.77[1] 71-69	10.19 65-65	65-63
R. W. Frey and W. R. Edington												
Per cent R. H. beginning and ending of drying	51	9.70 51-39	9.91 33-33	10.08 38-38	10.13 42-41	10.23 43-42	10.18[1] 62-53	10.40 66-38	10.46 44-39	10.63 48-36	11.06 31-25	46-38
T. D. Jarrell												
Per cent R. H. beginning and ending of drying	65	9.85 65-57	10.03 70-59	10.52 46-42	10.59 45-44	10.63 49-43	10.93 36-30	10.75[1] 45-48	10.82 49-45	10.92 43-39	11.03 42-33	49-44
Maximum		10.22	10.40	10.52	10.65	10.79	10.93	10.75	10.82	10.92	11.06	
Minimum		9.09	9.31	9.57	9.48	9.65	9.87	9.98	10.01	9.77	10.19	
Difference		1.13	1.09	0.95	1.17	1.04	1.06	0.77	0.81	1.15	0.87	
Average per cent moisture		9.71	9.90	10.15	10.21	10.32	10.43	10.46	10.44[1]	10.43[1]	10.74	
Average per cent relative humidity		56-51	52-49	50-47	49-47	48-45	51-46	57-48	55-52	59-53	50-44	

* Averages of three closely agreeing results.
[1] Lower than the previous 5-hour period of drying. Note that the R. H. is higher.

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the determination of moisture in leather, unless indeed it might be by a study of the effect of relative humidity during the time at which the determinations were made. There seemed to be much promise along this line, as indicated by the work reported at the last annual meeting by Veitch and Jarrell on "The Effect of Atmospheric Humidity on the Determination of Moisture in Leather,"[1] in which it was found that there was a difference of ± 0.5 per cent in the moisture results with a difference of 35 per cent in relative humidity.

Since the members of the Association were found to be heavily burdened with committee work, it was found difficult to secure extended co-operation in this work. Three other busy laboratories, however, found time to help, the work being made as light as possible to meet existing conditions.

Accordingly, in October, 1921, a sample of vegetable tanned sole leather was sent to several members of the Association who had expressed a willingness to co-operate in the work on the determination of moisture in leather. The entire sample was sawed, thoroughly mixed and placed in jars at the same time.

The following directions were sent out with the sample.

DIRECTIONS TO COLLABORATORS FOR A. L. C. A. WORK ON THE DETERMINATION OF MOISTURE IN LEATHER

A sample of sole leather marked Sample No. 1 is forwarded to you to-day by mail under separate cover, for the A. L. C. A. work on the determination of moisture in leather.

Please do not open the sample until ready to weigh out, and keep bottle closely stoppered between weighings.

Directions

Weigh rapidly and accurately three 5-gram portions of the sample into tannin dishes which, with watch glass covers, have been accurately weighed. Note and record the temperature and the relative humidity of the laboratory at the time of weighing out and at the beginning and ending of each period of drying. Dry the samples for ten 5-hour periods in the evaporator and dryer (which should contain no other material), the watch glasses being off the dishes during the drying. When each 5-hour period of drying is up, remove the dishes from the dryer, cover with the respective watch glasses, and place the dishes quickly in tight desiccators recently filled with fresh sulphuric acid, one dish to the

[1] *J. A. L. C. A.*, Oct., 1921, p. 547.

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desiccator. Allow to cool for one-half hour, weigh, and return to the desiccator until the next period of drying. Calculate the per cent loss in weight after each 5-hour period, and report your results on the accompanying report blank before the 15th of November.

Table I contains the results of the collaborative work.

Comments by Collaborators

L. Balderston: You will observe that on days when the relative humidity was high the samples increased in weight, over what they had shown on previous days when humidity was lower. I believe this means not absorption of water during weighing but during drying. More humid air passing through the drier permitted some absorption of moisture above what had taken place when the air was drier. I say this because there was no appreciable increase of weight when the covered dishes were allowed to stand in the balance case for some time after they were weighed. By adjusting the weights before removing the dish from the desiccator, I made a weighing in from ten to fifteen seconds. An additional minute made no difference in the figure. It looks as if fifteen hours' continuous drying would be enough. The final difference between the various sets of results are not so conspicuous as the difference at the end of the first and second 5-hour periods. May not this be due to differences of temperature between the evaporator used by different collaborators. It might be worth while in such work to take notice of temperatures at which the evaporator is maintained.

W. K. Alsop: Our ovens are in a separate room and entirely shut off from the rest of the laboratory. These tests were made in a small oven which holds about 40 dishes which average about 1° lower in temperature than our large ones which hold 200 dishes. I would prefer making these tests in a large oven but we could not spare it for the work. Our practice is to put the dishes in the oven in the afternoon, there being usually from four to five hundred of them. The oven room gets quite warm and of course there is a considerable moisture from the evaporation of the solution from the dishes. This work was done in the day-time after the room had been opened up and no other solutions were being evaporated. With the usual conditions of drying, the temperature in the oven we used would be about 1° higher. I have

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never favored long drying of leather samples in evaporators and dryers, preferring the shorter time in the hot air oven at 105° and believe more uniform results by different operators would be obtained in this way. We usually obtain higher results in moisture by drying 2 hours at 105°. The results in the hot air oven may perhaps be more correct.

R. W. FREY: Although the evidence is not clear cut, certain of these results would indicate an effect from humidity while drying. For example, the first decrease in per cent moisture occurred at the end of the 30-hour drying period and it will be noted that this was also the first period of drying under appreciably higher relative humidity. This is again well illustrated by comparison of the figures for the 45 and 50-hour drying periods respectively, when there was a decrease in relative humidity with a material increase in per cent moisture.

While it is fully appreciated that the relative humidity during the period of drying will exert an effect, sometimes material, it is nevertheless felt that relative humidity is not the chief contributing factor to wide discrepancies often, if not generally, occurring in a series of moisture results by a number of analysts. It is believed that equipment, procedure and technique play a far more important part.

One point, which would come under the procedure, might be worth citing, although, in view especially of the work of the last year on moisture, it might be considered too evident to mention. That is, the drying of moisture charges in an "evaporator and dryer" simultaneously with a number of total solids, soluble solids and non-tannin determinations. In this case the humidity in the dryer would surely be quite high for several hours of the overnight drying period and it would seem that decidely lower results for moisture would be obtained. It would be interesting to have some data on this and also to know how general this practice is in the tannery laboratories.

F. P. VEITCH and T. D. JARRELL: It is noted from this Table that whenever the results of the same analyst are lower than after the previous 5-hour period of drying, the relative humidity of the laboratory during that period was always higher than it was during the previous period of drying, although the difference is not striking because fluctuations in humidity were not great.

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The collaborator (Mr. Wright) who got the lowest moisture result (10.19 per cent) after 50 hours of drying, worked under the highest average relative humidity conditions (65-63 per cent).

Messrs. Frey and Edington, who worked under the lowest average relative humidity conditions (46-38 per cent), got the highest result, (11.06 per cent). This is in accordance with what was expected, yet the difference between these figures (0.89) is much greater than what was looked for since there was only about 20 per cent difference in the average relative humidity when these collaborators made the analysis. The difference between the maximum and minimum results of the various collaborators is great, ranging from 0.77 at the end of 35 hours' drying to 1.17 at the end of 20 hours' drying. This great difference is unquestionably not due entirely to humidity conditions but rather largely to the usual manipulative error of various chemists using various equipments. Special care was taken to mix thoroughly the leather before placing it in air-tight containers. About two months after sampling, Mr. Jarrell determined moisture at the same time and under identical conditions on charges taken from three different containers. The difference between the maximum and maximum results was but 0.06 per cent, showing that the great variation reported by the collaborators could not be due, even in part, to differences in moisture content of the leather in the bottles when opened.

In order to determine whether or not considerable variation in results will occur when the same chemist works with the same equipment but when the charges are weighed out at different times and under various humidity conditions and dried at irregular intervals, a series of experiments were conducted in this laboratory by Mr. Jarrell on the same sample of leather as was used in the collaborative work.

The procedure adopted was as follows:

SERIES A

Ten 5-gram charges from container "A" were weighed into weighing bottles numbered 1 to 10, inclusive, at one sitting in the laboratory, the relative humidity being 27 per cent, which is comparatively low.

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Series B

Immediately after weighing the charges from Series "A," ten 5-gram charges from container "B" were weighed into weighing bottles numbered from 11 to 20, inclusive, at one sitting in the constant temperature and humidity room at a relative humidity of 65 per cent, which is comparatively high.

Series C

At irregular intervals between December 20, 1921, and February 6, 1922, 5-gram portions in duplicate were taken from containers "C," "D," "E," "F," and "G" and weighed into weighing bottles at the prevailing humidity conditions of the laboratory.

Charges in bottles 21 and 22 were taken from container "C" on December 20, 1921 (R. H. 33 per cent);
23 and 24 from container "D" on December 28, 1921 (R. H. 31 per cent);
25 and 26 from container "E" on January 9, 1922 (R. H. 40 per cent);
27 and 28 from container "F" on January 27, 1922 (R. H. 31 per cent);
29 and 30 from container "G" on February 6, 1922 (R. H. 31 per cent).

In the groups given below the bottles for any one group were all dried simultaneously in the evaporator and dryer for one 15-hour period and then for two successive 5-hour periods on the dates given.

	Dates Dried.
Group 1.	
Bottles 1 and 2 of Series A Bottles 11 and 12 of Series B Bottles 21 and 22 of Series C	December 20, 1921, to December 22, 1921.
Group 2.	
Bottles 3 and 4 of Series A Bottles 13 and 14 of Series B Bottles 23 and 24 of Series C	December 28, 1921, to December 30, 1921.
Group 3.	
Bottles 5 and 6 of Series A Bottles 15 and 16 of Series B Bottles 25 and 26 of Series C	January 9, 1922, to January 11, 1922.
Group 4.	
Bottles 7 and 8 of Series A Bottles 17 and 18 of Series B Bottles 27 and 28 of Series C	January 27, 1922, to February 1, 1922.
Group 5.	
Bottles 9 and 10 of Series A Bottles 19 and 20 of Series B Bottles 29 and 30 of Series C	February 6, 1922, to February 10, 1922.

The results obtained by the procedure stated above are presented in Table II.

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TABLE II.—EFFECT OF WEIGHING AND DRYING AT DIFFERENT HUMIDITIES.

Period of drying Date dried	15 hrs. 12-20-21	20 hrs. 12-21-21	25 hrs. 12-22-21	15 hrs. 12-28-21	20 hrs. 12-29-21	25 hrs. 12-30-21	15 hrs. 1-9-22	20 hrs. 1-10-22	25 hrs. 1-11-22	15 hrs. 1-27-22	20 hrs. 1-31-22	25 hrs. 2-1-22	15 hrs. 2-6-22	20 hrs. 2-7-22	25 hrs. 2-10-22
	Group 1 Per cent moisture			Group 2 Per cent moisture			Group 3 Per cent moisture			Group 4 Per cent moisture			Group 5 Per cent moisture		
Series A, groups 1 to 5, bottles 1-10. Charges weighed at one sitting. Relative humidity, 27 per cent.	10.04	10.07	10.31	10.07	10.22	10.41	10.07	10.11	10.11	10.08	10.17	10.23	9.91	10.09	10.08
Series B, groups 1 to 5, bottles 11-20. Charges weighed at one sitting. Relative humidity, 65 per cent.	10.20	10.24	10.49	10.19	10.31	10.52	10.19	10.25	10.26	10.29	10.38	10.43	10.23	10.39	10.40
Series C, groups 1 to 5, bottles 21-30. Charges weighed at irregular intervals, from Dec. 20, 1921, to Feb. 6, 1922. Relative humidity varied from 31 to 40 per cent.	10.14[1]	10.19	10.44	10.13[2]	10.26	10.46	10.14[3]	10.22	10.22	9.95[4]	10.05	10.10	10.03[5]	10.18	10.18
Per cent relative humidity at beginning and ending of each period of drying.	33-38	38-34	29-25	31-42	42-26	28-25	43-39	39-30	42-37	28-37	38-34	34-34	29-37	35-27	41-34
Average per cent relative humidity during entire periods of drying.	33-32			34-31			41-35			33-35			35-33		

The above results are averages of closely agreeing duplicates.

[1] Relative humidity at time of weighing out charges, 33 per cent.
[2] Relative humidity at time of weighing out charges, 31 per cent.
[3] Relative humidity at time of weighing out charges, 40 per cent.
[4] Relative humidity at time of weighing out charges, 31 per cent.
[5] Relative humidity at time of weighing out charges, 31 per cent.

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Discussion of Table II.

Comparison of Series A and B. At the end of 15 hours' drying, the results show from 0.12 per cent (Group 2) to 0.32 per cent (Group 5) greater moisture content when the charges were weighed out at 65 per cent relative humidity than when they were weighed out at 27 per cent relative humidity. The difference at the end of 25 hours' drying ranged from 0.11 per cent (Group 2) to 0.32 per cent (Group 5).

Comparison of Series A and C. The difference between the results of series A and C range from 0.06 per cent (Group 2) to 0.13 per cent (Group 4) at the end of 15 hours' drying and from 0.05 per cent (Group 2) to 0.13 per cent (Groups 1 and 4) at the end of 25 hours' drying. This small difference is, no doubt, due to the slight variation in the relative humidity when the charges were weighed out.

Comparison of Groups within Same Series. By comparing results of the various groups within the same series after drying 25 hours, it is noted that the results in series A are:— maximum 10.41 per cent (Group 2), minimum 10.08 per cent (Group 5), difference 0.33; average 10.23 per cent. Series B, maximum 10.52 per cent (Group 2), minimum 10.26 per cent (Group 3), difference 0.26; average 10.42 per cent. Series C, maximum 10.46 per cent (Group 2), minimum 10.10 per cent (Group 4), difference 0.36; average 10.28 per cent.

Comparison of All Results. From an examination of the results comprising the entire groups of all series, the following data are revealed:

Drying 15 hours, maximum 10.29 per cent (series B, Group 4), minimum 9.91 per cent (series A, Group 5), difference 0.38; average 10.11 per cent.

Drying 20 hours, maximum 10.29 per cent (series B, Group 5), minimum 10.05 per cent (series C, Group 4), difference 0.34; average 10.21 per cent.

Drying 25 hours, maximum 10.52 per cent (series B, Group 2), minimum 10.08 per cent (series A, Group 5), difference 0.44; average 10.31 per cent.

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Comparison of Tables I and II.

The average of all results in Table I after drying for 15 hours is 10.15 per cent, the difference between the maximum and minimum being 0.95, while the average in Table II after 15 hours' drying is 10.11 per cent, the difference between the maximum and minimum being 0.38 per cent.

The average of all results in Table I after 25 hours' drying is 10.32 per cent, the difference between the maximum and minimum being 1.04. The average in Table II for the same period of drying is practically the same (10.31 per cent), the difference between the maximum and minimum being 0.44.

It should be noted that ordinary tannin dishes were used in making the moisture determinations in the collaborative work recorded in Table I, while ground stoppered weighing bottles (45 mm. wide and 65 mm. high) were employed for the work reported in Table II.

Veitch and Jarrell (*loc. cit.*) found that somewhat higher results, about 0.20 per cent in 15 hours' drying, were obtained by the use of tannin dishes. If this difference is added to the averages in Table II, the variation of results in the tables can be attributed to the humidity conditions at the time the determinations were made and to other manipulative errors due to a probable difference in equipments used by the various collaborators. The average results of the two tables are fairly close, but the variation between the individual collaborators is considerable. The individual results by the same analyst working with the same equipment, but under somewhat different humidity conditions, and the drying carried on at various times ranging over a period of about seven weeks, are remarkably close in comparison with those obtained by several chemists working in different laboratories.

Referring to Mr. Alsop's suggestion to dry at 105° C. in a hot air oven, Mr. Jarrell and the Chairman, in conducting the work on the effect of humidity reported last year, found that even after drying in the electric oven for 70 hours, by which time the loss had become fairly steady, there was a sudden and decided increased loss on drying the samples at 105° C. in an air oven. This showed that the increase of but 5° or 6° in drying temperature introduces another set of equilibrium conditions. Mr. Jar-

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rell has dried the sample of leather sent out this year for the moisture work in an electric oven at 105° C., using covered tannin dishes. The results were as follows, with the relative humidity between 27 and 30 per cent:

		Per cent
2 hours' drying,		9.82
		9.89
		9.58
		9.62
	Av.	9.72
4 hours' drying,		10.13
		10.18
		9.88
		9.93
	Av.	10.03
6 hours' drying,		10.23
		10.29
		10.00
		10.03
	Av.	10.14

Duplicates dried in the evaporator and dryer at the same time gave, on 5 hours' drying, 9.80 per cent moisture.

It is interesting to note the lack of agreement between the two pairs of results where all the weighings were made at the same sitting and both pairs dried in the oven at the same time. The individual results maintain the same order throughout the three periods of drying. The weighings were made in the order given, always placed in the oven in the same order, the first two immediately behind the thermometer in the center, the last two immediately in front of the thermometer. This relationship should furnish a clue to the difference obtained by different analysts. On this sample at least, the moisture, on drying 6 hours at 105° C., was about the same as on drying 12 hours in the water oven. The relative humidity, when the dryings were made at 105° C., was 27-33 per cent and 57-70 per cent when the sample was dried in the water oven. These results do not indicate any marked advantage in drying at 105° C. in an air oven. In this connection it will be recalled that Veitch and Jarrell's work last year showed that the highest moisture results were obtained in the vacuum oven at 97 to 98° C., as compared with the electric oven at 100° C.,

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which in turn gave higher results than drying in the evaporator and dryer at 99° C., which in turn gave higher results than the vacuum at 70° C.

The correlation that exists between the relative humidity and percentage of moisture found by each analyst clearly shows that relative humidity affects the determination of moisture in leather. On the other hand, the differences between the results reported by different laboratories show that some other factor or factors are much more influential.

The results are of the same general nature as those usually obtained in collaborative work on moisture determination in similar materials, and leave unsettled the primary causes for the differences. The results do emphasize again, however, the absolute necessity for the utmost care in moisture determination. All established precautions must be observed. The temperature of drying must be fully maintained, samples must be handled rapidly, desiccators must be tight, the drying oven should be well ventilated and its atmosphere not charged with moisture. The concordance of results, except as influenced by relative humidity, by individual analysts leaves little question but that local and unknown conditions were the chief factors in determining the variations reported.

The results also are in agreement with those reported last year by Veitch and Jarrell, and indicate that 15 hours' drying at temperature of boiling water is insufficient.

No consideration was given to the method for the preparation of samples. This is a very important matter since it has been shown on numerous occasions that the way in which the sample has been prepared decidedly affects not only the moisture but also other analytical figures. There are two main factors here; one, the heat generated in preparing the sample which may dry it considerable; the other, the relative humidity existing at the time the sample is prepared. If the sample remains exposed long enough after preparation, this latter factor will control the moisture in the prepared sample. If the sample is bottled at once, it will affect the moisture to a greater or less extent. The matter of the preparation of samples of leather for analysis, including the effect of methods of preparation on moisture content and composition, would serve admirably for a number of theses by college or university students of a practical bent.

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Conclusions.

There are unknown factors more influential than relative humidity that affect the determination of moisture in leather by different analysts.

Fifteen hours' drying in a water oven (evaporator and dryer) is not sufficient to remove all apparent moisture.

No method or equipment for drying, so far used, has shown positive superiority in concordance or accuracy of results.

There is need for a procedure that will give acceptable results within a working day.

Recommendations.

Since an analyst can check his own results quite acceptably, it is apparent that the differences between different analysts are due to differences in procedure. It is therefore recommended that a study of differences in procedure in the same method by some member of the association be encouraged to the end that the essential details necessary to secure concordant and accurate results may be fully known.

Study of vacuum oven at 100° C. and 105° C., water oven at 99-100° C., and air or electric oven at 105° C. under the same humidity conditions, with the view to developing a procedure that can be completed in a working day, should be continued. The Chairman and Mr. Jarrell are now working on this matter and it is hoped to have the results ready in time to be of service to next year's committee.

Individual study of methods for the preparation of leather for analysis is recommended.

The Chairman is indebted to Mr. T. D. Jarrell, of the Bureau of Chemistry, for assistance in outlining the work and for his pains-taking preparation of samples and analytical work.

DETERMINATION OF EPSOM SALTS IN LEATHER—1922 COMMITTEE REPORT

R. W. Frey, Chairman

The following discussion and directions, including samples mentioned therein, were sent to each member of the committee.

Discussion

It is believed that the work of last year's committee (*J. A. L. C. A.*, **16**, 595, 1921) sufficiently proved that the volumetric de-

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termination of magnesium gives as satisfactory results as does the gravimetric method. In most instances there are no significant differences between the results of any one member by both the gravimetric and volumetric methods. It does seem, however, that the results show between different members of the committee greater discrepancies than are desirable, thus indicating sources of error or difference common to both the gravimetric and volumetric procedures. Aside from technique or manipulation, the conditions for precipitation of magnesium as ammonium magnesium phosphate would suggest a probable source of error and it has been deemed advisable to study these conditions this year. To reduce the work, only the gravimetric method will be used, since it seems safe to assume, as pointed out above, that the volumetric method will give the same results. Your opinion on this, however, is sought.

The generally accepted standard procedure for the accurate precipitation of ammonium magnesium phosphate requires either previous destruction of excess of ammonium salts or the removal of their influences by double precipitation, avoiding in the second one, excess of ammonium salts and precipitant. To eliminate these extra operations a method for single hot precipitation without previous removal of ammonium salts has lately received considerable attention and favorable comment as giving reasonably accurate results. Now it is believed that the usual practice in leather analysis is to make only a single cold precipitation without regard to ammonium salts and precipitant. It seems therefore worth while to compare all three of the above sets of conditions. It may be however that at even the maximum concentration of magnesium generally met with in leather analysis an excess of ammonium salts and precipitant does not exert sufficient influence to warrant their removal; or it may be that the concentration of magnesium can be so reduced as to make this the case. The outline given below has been planned to include these points.

Directions and Samples

The two samples of leather marked "Leather No. 1" and "Leather No. 2" are to be used for this work. Weigh all charges of leather accurately, yet rapidly, to avoid appreciable change in moisture content.

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Weigh four 10-gram charges of each leather and proceed with each charge as follows: Ash; determine the ash; carefully moisten the ash with H_2O, avoiding loss while doing so; add 15 cc. concentrated HCl; wash into a beaker, dilute to 50-75 cc.; add 2-3 drops of concentrated HNO_3; gently boil for a few minutes or heat on a steam bath for 15 minutes. Without filtering off insoluble matter add NH_4OH (approximately 1 to 1) slowly with constant stirring until nearly neutral but still slightly acid, then dilute the NH_4OH (about 3 or 4 to 1) and precipitate with a very slight excess of it; boil for a couple of minutes; filter and wash the precipitate thoroughly with hot H_2O. If necessary, evaporate the filtrate to 175-200 cc. and make ammoniacal (about 1 cc. NH_4OH); boil gently and add slowly with constant stirring 10 cc. of a saturated ammonium oxalate solution; cover and let stand 2 hours or longer on a steam bath or in a warm place. Quantitatively transfer all four solutions together with precipitate to a 1,000 cc. volumetric flask; cool to 20° C., and fill the flask to mark with distilled water and mix thoroughly. Filter through double dry quantitative paper, making sure that filtrate is absolutely clear. Pipette three 250 cc. aliquots and three 50 cc. aliquots from the filtrate. Evaporate the 250 cc. aliquots to 200 cc. and dilute the 50 cc. ones to 200 cc.

Double cold precipitation.—With one 250 cc. aliquot proceed as follows: (a) Make slightly acid with HCl (methyl orange); cool to room temperature if necessary; add 15 cc. saturated sodium ammonium hydrogen phosphate solution (pure microcosmic salt should be used; the saturated solution should not be very old and must always be filtered before using); while stirring vigorously add a few drops of NH_4OH just until precipitation starts or until faintly ammoniacal; let stand 15 minutes; add with stirring 5 cc. concentrated NH_4OH; cover and let stand overnight at room temperature. (b) Carefully and thoroughly decant the supernatant solution through a well prepared Gooch crucible, leaving the precipitate in the beaker; dissolve the precipitate in the minimum quantity of HCl; dilute to 100-150 cc.; add 3-5 drops of saturated sodium ammonium hydrogen phosphate solution; with constant stirring add NH_4OH drop by drop just until precipitation starts or until faintly ammoniacal; let stand 15 minutes; add with stirring 5 cc. concentrated NH_4OH; cover; and

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let stand overnight at room temperature. Filter into the Gooch crucible through which the supernatant solution from the first precipitation was decanted; (c) wash the precipitate free from chlorides with dilute 1 to 9 ammonia water (1 part concentrated NH_4OH sp. gr. 0.90 to 9 parts H_2O); finally just moisten the precipitate with a few drops of a solution of approximately 50 per cent NH_4NO_3 in 1 to 9 ammonia water. Dry the precipitate; ignite gently at first, then cover the crucible and ignite intensely over the hottest flame of a Bunsen or Meker for 20-30 minute intervals until constant in weight (if porcelain Gooches are used a blast may be necessary). Weigh as $Mg_2P_2O_7$; multiply by 2.2135 to convert to $MgSO_4.7H_2O$; enter the result as per cent $MgSO_4.7H_2O$ on 10 grams of leather.

Dilute one of the 50 cc. aliquots to 200 cc. and carry it through exactly as directed above under double cold precipitation, except use only 5 cc. of saturated sodium ammonium hydrogen phosphate instead of 15 cc. Enter the result as per cent $MgSO_4.7H_2O$ on 2 grams of leather.

Single cold precipitation.—With one 250 cc. aliquot proceed exactly as under (a) of double cold precipitation, then filter into a Gooch crucible and proceed as under (c) of double cold precipitation.

Repeat with one of the 50 cc. aliquots after diluting it to 200 cc. Use only 5 cc. of saturated sodium ammonium hydrogen phosphate instead of 15 cc.

Enter the results in their respective columns.

Single hot precipitation.—With the third 250 cc. aliquot proceed as follows: Add 5 cc. concentrated NH_4OH; bring to gentle boiling; add 15 cc. of saturated sodium hydrogen phosphate solution and heat at the boiling temperature for several minutes. (If necessary, induce precipitation by rubbing the side of the beaker with a rod and when precipitation starts it may be necessary to constantly stir to prevent bumping). Add while stirring 5 cc. of concentrated NH_4OH diluted with 5 cc. of H_2O; remove from the flame; cover the beaker and let stand overnight. Filter into a Gooch crucible and proceed as under (c) of double cold precipitation.

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Repeat with the third 50 cc. aliquot after diluting it to 200 cc. Use only 5 cc. of saturated sodium ammonium hydrogen phosphate instead of 15 cc.

Enter the results in their respective columns.

Results.

The results of the members of the committee are given in the accompanying table.

A copy of this table, with the preliminary comments and the following proposed provisional method for the determination of Epsom salts in vegetable tanned leathers, was then sent each committee member with the request to submit final comments and to vote definitely for or against "single cold" or "single hot" precipitation of magnesium and for or against the rest of the method as outlined.

Proposed Provisional Method for the Determination of Epsom Salts in Vegetable Tanned Leathers

Ash 5 or 10 grams of leather; carefully moisten ash with H_2O; add 15 cc. concentrated HCl; wash into a beaker; dilute to 50-75 cc.; add 2-3 drops of concentrated HNO_3; gently boil for a few minutes or heat on a steam bath for 15 minutes. Without filtering off insoluble matter add NH_4OH (approximately 1 to 1) slowly with constant stirring until nearly neutral but still slightly acid, then add dilute NH_4OH (about 3 or 4 to 1) and precipitate with a very slight excess of it. (If the NH_4OH precipitate does not have the characteristic reddish brown color of ferric hydroxide and there is known to be sufficient NH_4Cl present to hold in solution all magnesium, redissolve without filtering in HCl, add a few drops of pure ferric chloride solution and reprecipitate with NH_4OH). Boil for a few minutes; filter and wash the precipitate thoroughly with hot H_2O. If necessary, evaporate the filtrate to 175-200 cc. and make ammoniacal (about 1 cc. NH_4OH); boil gently and add slowly with constant stirring 10 cc. of a saturated ammonium oxalate solution; cover and let stand 2 hours or longer on a steam bath or in a warm place. Quantitatively wash solution and precipitate into a 250 cc. volumetric flask; cool to 20°-25° C.; fill to mark with distilled H_2O and mix thoroughly. Filter through quantitative paper making sure that filtrate is absolutely clear. Pipette an aliquot

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COMMITTEE RESULTS ON DETERMINATION OF EPSOM SALTS IN LEATHER.

Collaborator	Leather No. 1							Leather No. 2						
	Per cent $MgSO_4 . 7 H_2O$ found by							Per cent $MgSO_4 . 7 H_2O$ found by						
	Per cent ash	Double Cold		Single Cold		Single Hot		Per cent ash	Double Cold		Single Cold		Single Hot	
		on 10 grams	on 2 grams	on 10 grams	on 2 grams	on 10 grams	on 2 grams		on 10 grams	on 2 grams	on 10 grams	on 2 grams	on 10 grams	on 2 grams
L. A. Cuthbert Elk Tanning Co.	2.23	5.06	5.01	5.15	4.94	5.06	5.05	2.33	6.00	5.92	6.13	5.92	5.99	5.95
F. F. Marshall Kistler Leather Co.	2.26	4.95	4.98	5.01	4.92	5.01	4.95	2.30	6.08	6.12	6.14	6.06	6.07	6.15
L. E. Stacey and L. M. Nelson C. C. Smoot & Sons Co.	2.21	4.69	4.78	4.78	4.79	4.78	4.79	2.25	6.02	6.17	6.02	6.15	6.03	6.02
L. E. Stacey and L. M. Nelson C. C. Smoot & Sons Co.	2.31		4.80		4.98		4.85							
L. R. Leinbach Leather and Paper Lab.	2.34	5.10	5.07	5.30	5.06	5.12	5.16	2.46	6.10	5.89	6.25	6.08	6.17	5.98
R. W. Frey Leather and Paper Lab.	2.31	5.08	4.85	5.30	5.15	5.19	4.93	2.35	6.05	6.01	6.16	6.04	6.08	6.04
Average	2.28	4.98	4.92	5.11	4.98	5.03	4.96	2.34	6.05	6.02	6.14	6.05	6.07	6.03
Maximum	2.34	5.10	5.07	5.30	5.15	5.19	5.16	2.46	6.10	6.17	6.25	6.15	6.17	6.15
Minimum	2.21	4.69	4.78	4.78	4.79	4.78	4.79	2.25	6.00	5.89	6.03	5.92	5.99	5.95
Difference	0.13	0.41	0.29	0.52	0.36	0.41	0.37	0.21	0.10	0.28	0.22	0.23	0.18	0.20

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equivalent to 2 grams of the original leather and dilute to about 150 cc. Precipitate the magnesium either by

(A) *Single cold precipitation.*—Make slightly acid with HCl (methyl orange); cool if necessary; add a slight excess of clear saturated sodium ammonium hydrogen phosphate solution (5 cc. generally sufficient); while stirring vigorously, add a few drops of NH_4OH just until precipitation starts or until faintly ammoniacal; let stand 15 minutes; add with stirring 5 cc. concentrated NH_4OH; cover and let stand overnight at room temperature. Or by

(B) *Single hot precipitation.*—Add 5 cc. concentrated NH_4OH; bring to gentle boiling; add a slight excess of clear saturated sodium ammonium hydrogen phosphate solution (5 cc. generally sufficient); heat at the boiling temperature for several minutes. (If necessary, induce precipitation by rubbing sides of the beaker and when precipitation starts it may be necessary to constantly stir to prevent bumping). Add while stirring 5 cc. concentrated NH_4OH diluted with 5 cc. of H_2O; remove from the flame; cover and let stand overnight at room temperature.

After standing overnight proceed either by the gravimetric or volumetric method.

Gravimetric: Filter through a well prepared Gooch; wash the precipitate free from chlorides with 1 part concentrated NH_4OH sp. gr. 0.90 to 9 parts H_2O; finally just moisten the precipitate with a few drops of a solution of approximately 50 per cent NH_4NO_3 in 1 to 9 ammonia water; dry; ignite gently at first, then cover the crucible and ignite intensely for 20-30 minute intervals until constant in weight; weigh as $Mg_2P_2O_7$; multiply by factor to convert to $MgSO.7H_2O$ and express as per cent on 2 grams of leather.

Volumetric: Filter clear, through close quantitative paper; wash the precipitate free from chlorides with 1 part concentrated NH_4OH sp. gr. 0.90 to 9 parts H_2O; remove excess of ammonia wash water either by washing 3 or 4 times with neutral 60 per cent by volume methyl alcohol solution; or by spreading out the filter paper with its precipitate on to coarse absorbent filter paper for a couple of minutes and then on to a watch glass

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and dry for 1 hour at 50° C., (if 60° C. is exceeded, determination must be discarded); or by air drying the opened out filter with its precipitate overnight at room temperature. After removal of ammonia transfer paper with its precipitate to a beaker or flask; moisten with H_2O; thoroughly disintegrate the paper; add an accurately measured excess of standardized 0.10 N H_2SO_4 and 2 or 3 drops of methyl orange (0.1 per cent alcoholic solution). Dilute to about 100 cc. and determine excess of acid by titrating with 0.10 N NaOH to a clear yellow without any suggestion of pink. One cc. of 0.10 N H_2SO_4 is equivalent to 0.0123 grams $MgSO_4.7H_2O$. Calculate to grams $MgSO_4.7H_2O$ and express as per cent on 2 grams of leather.

Comments

The following comments have been abstracted from considerable correspondence.

L. A. Cuthbert, Elk Tanning Company: With the exception of the "single cold" precipitation, I obtained results when precipitating from the 10 gram and 2 gram aliquots which agreed very closely. Using the "single cold" method the difference in the case of each leather amounted to 0.21 per cent. My objection to the "double cold" precipitation is that it takes too much time to complete the determination.

After reviewing the work of the committee and the comments I am of the opinion that we should include both the "single cold" and "single hot" precipitations. Therefore, I wish to vote for the method as outlined including both "A" and "B." The results are all in such close agreement that it is impossible to say which of the three methods is the best. Since this is the case the method which is most convenient would naturally be chosen. As far as convenience is concerned there is not much choice between "A" and "B" and I believe that by including both in the provisional method the choice of making the precipitation from a 2 gram sample or a 5 to 10 gram sample could be left to the operator.

The work of the 1921 committee proved that the volumetric method gave almost exactly the same results as the gravimetric and I do not believe that it is necessary to do further work on the comparison of these methods.

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L. R. LEINBACH, Leather and Paper Laboratory, Bureau of Chemistry: It is evident that the averages reported on the 2 gram aliquots by all three methods of precipitation are in very substantial agreement. While probably both the "single hot" and "double cold" methods are preferable theoretically, especially when determining high percentages of magnesium, it is more than likely that for the determination of magnesium in leather, the "single cold" precipitation affords the desirable degree of accuracy. The "double cold" method is ruled out because of the time it consumes. The "single cold" offers some advantages of manipulation over the "single hot" and therefore it is to be preferred, but only on the 2 gram aliquot basis. The 10 gram aliquot is inadvisable except for small quantities of magnesium. I hereby vote for the method as outlined and for the "single cold" method of precipitation.

F. F. MARSHALL, Kistler Leather Co: The results from the three methods outlined are closer than might be expected and any one of them could be used as an official method. We find that the "double cold" precipitation method on both the 2 and 10 gram aliquots gives results closest to the general average. The principal objection to this method would be the length of time needed to complete the work. With reference to the "single hot" method the precipitate adheres closely to the beaker and stirring rod; it is difficult to wash off and further, when wet, is transparent and difficult to see.

We quite agree with you as to the determination being made on the 2 gram aliquot and cast our vote in favor of the method as outlined for "single cold" precipitation under "A," the choice of the gravimetric or volumetric procedure to be left to the operator.

L. E. STACY AND L. M. NELSON, C. C. Smoot and Sons Co.: In looking over the results it is interesting to note how closely the different methods check each other. The ammonium salts in any of the methods do not appear to exert any appreciable influence on the ammonium magnesium phosphate precipitate, the final results checking satisfactorily and within experimental error. Although Gibbs (*Am. J. Sci.*, 3, 5, 114) recommends precipitation from a boiling solution, we would give preference to the "single

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cold" precipitation for general analysis. We wish to be recorded as voting in favor of the method as outlined using the "single cold" precipitation given under "A."

CHAIRMAN: All results by all collaborators show surprisingly good agreement, with the exception of the first set of figures by Stacy and Nelson on Leather No. 1. Upon repeating the work in part, they obtained results in good agreement with those of the other members of the committee. Stacy and Nelson are not able to explain their rather low results obtained the first time.

While it may be said that, for practical purposes, all three methods of precipitation give the same results, yet it will be noted that there is a slight, though rather consistent, tendency for high results by "single cold" precipitation on the aliquots representing 10 grams of leather. It is believed, too, that in the ordinary run of routine work where generally due regard to details and to the amount of ammonium salts and precipitant is not given, this tendency for high results on the full charge of leather would be appreciably greater. Reducing the concentration of magnesium, as by taking a 2 gram aliquot, considerably reduces the tendency for high figures and it will be observed that the results by "single cold" precipitation on the 2 gram aliquot are almost identical with those by either "double cold" or "single hot" precipitation. For this reason and also because the "single cold" is slightly more convenient than the "single hot," the chairman would recommend the "single cold" precipitation. It should be emphasized, however, that this recommendation is made only on the provision that the method as herein proposed, specifying a 2 gram aliquot of the original charge, be adopted. If the method is modified to include determination of magnesium on the full charge of either 5 or 10 grams of leather then the "single hot" precipitation is recommended.

It may be well to mention one point in connection with the determination of magnesium, which though well known may not be fully appreciated. If, in the precipitation of calcium with ammonium oxalate, the magnesium content is high, the volume of the solution small, and the period of heating and standing unnecessarily prolonged, large quantities of magnesium may be thrown down as difficultly soluble magnesium oxalate and con-

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sequently give low magnesium results. There would seem no likelihood of this, however, if the quantities and concentrations given in the method are followed.

In the method herewith proposed, the volumetric procedure has been incorporated from the work of last year's committee which showed practically the same results by both the gravimetric and volumetric procedures.

Recommendation

Since the committee is pretty generally agreed, it is recommended that the method as herein outlined for the determination of epsom salts in vegetable tanned leather using "single cold" precipitation as given under "A" be provisionally adopted.

DETERMINATION OF GLUCOSE IN LEATHER— 1922 COMMITTEE REPORT

I. D. Clarke, Chairman, pro tem.

The use of sodium phosphate for the removal of lead from the clarified extract was investigated by last year's committee[1] and the recommendation was made that further work be done since the results were not conclusive. For the committee work this year this same line of work was followed, using directions which were prepared by Mr. J. S. Rogers, the chairman of this committee until he found it necessary to resign a short time ago.

Two samples of leather, one oak tanned containing no added glucose or epsom salts, and the other chestnut tanned, containing both glucose and epsom salts, were sent out. Each committee member was asked to furnish, for his own use, one sample of leather which contained no added glucose or salts. A sample of Merck's pure dextrose, found by analysis to be 97.8 per cent pure, was also sent out.

Directions and samples were sent to L. A. Cuthbert, Elk Tanning Co; S. K. Johnson, Phoenix Leather Co; L. M. Whitmore and G. V. Downing, Leas and McVitty, Inc., and J. C. Dickson, Champion Fiber Co.

The directions were as follows:

[1] *J. A. L. C. A.*, 16, 480 (1921).

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Special Solutions Required

Sodium phosphate solution, $Na_2HPO_4.12H_2O$. Dissolve 500 grams of Merck's reagent sodium phosphate in 600 cc. distilled water on steam bath, dilute to about one liter, mix, cool to 25° C. and make to volume, filter if necessary. In case this phosphate crystallizes out on standing, warm, dissolve and cool to 25° C. before using.

Sodium hydroxide solution.—Dissolve 250 grams pure NaOH and dilute to 500 cc.

Preparation of Sugar Solutions

Dissolve 1.228 g. of Merck's highest purity dextrose (equivalent to 1.2 grams of actual dextrose as determined by analysis) in distilled water and dilute to one liter and mix thoroughly. Pipette three 200 cc. portions in 500 cc. Erlenmeyer flasks numbered one, two and three. To flasks number one and two, add 25 cc. of distilled water and to flask number three, add 25 cc. of lead acetate solution. (As there is no tannin present in this case, use 15 cc. of saturated lead acetate solution and 10 cc. of water). Mix the solution and filter through a 15 cm. filter, collect 185 cc. Pipette 180 cc. of the filtrate into a flask and add for numbers one and two 30 cc. of water, and for number three 30 cc. of sodium phosphate solution; mix and filter, returning until clear. Collect 180 cc. For number one pipette 175 cc. of the filtrate into a 200 cc. graduated flask, make to volume and filter through a double filter. For numbers two and three, pipette 175 cc. into an Erlenmeyer flask, add 5 cc. of concentrated HCl, hydrolyze for two hours under reflux condenser, neutralize with NaOH solution from a burette, using one drop of phenolphthalein as indicator, and add ½ cc. in excess. Transfer to a 200 cc. graduated flask, make to volume at room temperature, mix and filter through a double filter. From this point on treat all solutions alike, making the reduction by the regular official procedure. Duplicate reductions will thus give a total of six sugar determinations for this section of the work.

Preparation of Leather Extracts

Extract all three samples of leather by the regular official method, using a Reed-Churchill extractor if available. Prepare

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five dry one-liter flasks and number them, one to five. In flask number two, place 1.228 g. of Merck's highest purity dextrose equal to 8 per cent actual dextrose on the leather and 1.05 g. of epsom salts equal to 7 per cent on the leather. Fill the flask to the mark with the leather extract obtained from sample number one and mix thoroughly. Place the remainder of the leather extract from sample number one in flask number one. Fill flask number three with leather extract obtained from sample number two. In flask number five place 0.614 g. of Merck's highest purity dextrose and 0.600 g. of epsom salts equal to 4 per cent on the leather. Then fill the flask to the mark with leather extract obtained from sample number three and mix thoroughly. Place the remainder of the extract obtained from sample number three in flask number four. This will give five leather extracts for analysis.

Analysis

Upon the five leather extracts make duplicate clarifications and duplicate reduction on each clarification. This gives ten clarifications and twenty final sugar determinations. Use the following procedure for the clarifications and reductions:

Place 200 cc. of leather extract of analytical strength in a 500 cc. flask, add 25 cc. of saturated solution of normal lead acetate, mix thoroughly, and filter on a 15 cm. plaited filter. (Funnels and beakers must be kept covered to prevent evaporation). Allow to drain until 190 cc. have been collected. Pipette 180 cc. of the filtrate and add 30 cc. of 50 per cent $Na_2HPO_4.12H_2O$, mix frequently during 15 minutes and filter, returning until clear. Collect 180 cc. Pipette 175 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for two hours, cool, neutralize with concentrated NaOH, using one drop of phenolphthalein as indicator, adding 0.5 cc. in excess, cool to room temperature if necessary, transfer to 200 cc. graduated flask, make to volume, mix thoroughly and filter through a double filter. Pipette 50 cc. for reduction with Fehling solution, using the regular official procedure as given in the A. L. C. A. method.

The results obtained are given in Tables I and II.

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TABLE I.—SUGAR SOLUTIONS

	Sugar solution untreated % on basis of 8% on leather	Sugar solution hydrolysed but not clarified % on basis of 8% on leather	Sugar solution clarified and hydrolysed % on basis of 8% on leather
L. A. Cuthbert, Elk Tanning Co.	7.94	8.00	8.52
	7.94	8.00	8.48
	7.94	8.02	8.58
	7.98	7.98	8.62
Average	7.95	8.00	8.55
I. D. Clark, Bureau of Chemistry	7.93	7.80	8.04
	7.88	7.83	8.03
	7.82	7.70	8.08
	7.83	7.77	8.03
Average	7.86	7.78	8.05
General average	7.91	7.89	8.30
Highest individual result	7.98	8.02	8.62
Lowest individual result	7.82	7.70	8.03
Greatest difference	0.16	0.32	0.59

TABLE II.—LEATHER EXTRACTS

	Extract from leather No. 1		Extract from leather No. 2	Extract from leather furnished by Committee Member	
	Alone	+ 8% Glucose + 7% Epsom salts		Alone	+ 4% Glucose + 4% Epsom salts
	%	%	%	%	%
L. A. Cuthbert, Elk Tanning Co.	0.83	8.82	8.32	1.90	5.60
	0.85	8.78	8.26	2.00	5.76
	1.06	8.90	8.38	1.86	5.68
	0.96	8.94	8.36	1.92	5.64
Average	0.93	8.86	8.33	1.92	5.67
Greatest difference	0.23	0.16	0.12	0.14	0.16
± Error		—0.07			—0.25
I. D. Clark, Bureau of Chemistry	0.69	8.18	8.06	0.49	4.41
	0.54	8.20	8.03	0.49	4.60
	0.56	8.42	7.96	0.44	4.60
	0.61	8.49	8.03	0.42	4.48
Average[1]	0.60	8.32	8.02	0.46	4.52
Greatest difference	0.15	0.31	0.10	0.07	0.19
± Error		—0.28			+0.06
	0.66	8.49	8.17	0.28	4.43
	0.56	8.54	8.19	0.37	4.45
	0.46	8.54	8.02	0.30	4.52
	0.49	8.52	8.02	0.28	4.45
Average[2]	0.54	8.52	8.10	0.31	4.46
Greatest difference	0.20	0.05	0.17	0.09	0.09
± Error		—0.02			+0.15
General average	0.69	8.57	8.15		
Maximum	1.06	8.94	8.38		
Minimum	0.46	8.18	7.96		
Greatest difference	0.60	0.76	0.42		

[1] Used 150 cc. for hydrolysis instead of 175 cc.—analysis Mar. 30, 1922.
[2] Used 160 cc. for hydrolysis instead of 175 cc.—analysis April 7, 1922.

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Comments

Mr. Cuthbert.—By the use of sodium phosphate solution the lead appears to be completely removed from the solution before hydrolyzing. No precipitate was obtained upon neutralizing with NaOH. The method as outlined seems satisfactory though I would favor taking a larger volume of solution at the start in order to save time and to take a smaller volume of the filtrate for hydrolyzation for the same reason.

Chairman pro tem.—The results with sugar solutions seem to indicate that the process of clarification adds something to the solution which is precipitated with or retained by the cuprous oxide for the results are somewhat higher if the solution has been treated as for clarification.

It was found to be very difficult to pipette the phosphate solution at 25° on account of its tendency to crystallize. If the solution was heated to 80° or 90° and then cooled very slowly, it could be used at 25° if protected from dust, otherwise it was necessary to pipette at 30°. The error introduced from this source is however negligible. The density of the phosphate solution, referred to water at 25°, was determined with sufficient accuracy for the present purpose and was found to be at 25° 1.1846, at 30° 1.1829, and at 35° 1.1801. Then 30 cc. measured at 35° would have a volume of 29.88 cc. at 25° and this would introduce an error of less than 0.005 per cent.

Considerable difficulty was experienced in obtaining 175 cc. for hydrolysis when working with leather extracts. Only 160 or 170 cc. would collect in three hours and it would therefore seem desirable either to start with a larger volume of extract or to use a smaller volume for hydrolysis.

Very little progress seems to have been made this year for, as was the case last year, there is considerable variation in the duplicates and in the results by the two analysts, although the averages agree very well.

It is recommended that this work be continued in order to determine the cause for and to eliminate this variation in duplicates and that other volume relations than those used here be tried.

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ANALYSIS OF CHROME LEATHER— 1922 COMMITTEE REPORT

L. Balderston, Chairman

The number of members volunteering for this Committee was small, and included no representative of the tanners of chrome goat or other light leathers. The conditions thus seeming unfavorable to any attempt to formulate a complete scheme for chrome leather analysis, only two points were taken up. The two provisional methods for chrome determination have been found by some observers to give different results. An article by Mr. T. P. Hou published in the JOURNAL[1] seems to call in question the comparability of the two methods, but he does not explain how he obtains the "solution" with which he deals when sodium peroxide is used.

Page 367, 13th. line from bottom; "the figure for chromium as determined by this volumetric method when the ash of the leather was fused with a mixture of K_2CO_3, Na_2CO_3 and $Na_2B_4O_7$ did not agree with that obtained by the same method when the chromic salt solution obtained from the same sample was oxidized with Na_2O_2 added to the solution."

The provisional method does not contemplate oxidizing any solution with Na_2O_2. The ash of the leather is fused with sodium peroxide, in an iron crucible, and by this means all the chromium is converted into chromates of sodium and potassium. After this alkaline melt is dissolved in water, the solution, with a heavy precipitate of ferric hydroxide, is boiled for 20 minutes or more to decompose any remaining Na_2O_2. Mr. Hou claims that this boiling does not always completely decompose the Na_2O_2. On this point the work of the present committee does not bear out Mr. Hou's contention.

The testing out of the two methods of chrome determination was one of the two points taken up, and the other was the matter of free acid. Just after the directions were sent out, there appeared an article by W. R. Atkin in *The Journal of the Society of Leather Trades' Chemists* on this subject.[2] This article is evidently merely a preliminary discussion, as no leather samples were used in the work described.

[1] 1920, page 367 ff.

[2] March number, page 89.

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Messrs. Frey, Cuthbert, and Wallace consented to serve on the committee, and Mr. Wallace kindly furnished two large samples of heavy leather which had been sawed. From these, after thorough mixing, bottles were filled and sealed. The following directions were sent:

A. L. C. A. Committee on Chrome Leather Analysis, 1922:

The Chairman believes it is not possible to present anything conclusive from so small a committee and one on which the tanners of light leathers are not represented. He proposes therefore to ask for some work which may help in determining how well the two methods of chrome determination now included in our provisional methods agree with each other, and for opinions on the subject of determining free acid. The provisional method for free mineral acid in vegetable tanned leather is not applicable to chrome leather.

Two samples of leather have been sent to each member. A is heavily loaded with salts of barium; B is a straight chrome leather with little or no load. Please determine moisture on each by the A. L. C. A. official method, 16 hours at 95 to 100° C.

Please also determine chrome in each by both methods, *a*, *b*,[3] The leather is best ashed in a smooth porcelain dish some 6 cm. in size, at low red heat. In method *a*, instead of powdered borax glass, borax may be used: 3 grams placed alone in a platinum crucible first, and heated to quiet fusion; then cool and add the ash and 3 grams of mixed carbonates, and fuse 30 minutes over a burner of the Meker type. In treating Leather A by this method there is a heavy residue on dissolving the melt in hot dilute HCl, consisting largely of barium sulphate. Do you think there is likely to be any advantage here in a second fusion?

In using method *b*, it is important not to use much excess of peroxide, certainly not more than 4 grams. In this fusion, a colloid sol of ferric hydroxide sometimes forms, and sometimes a green solution which seems to be an alkaline ferrate. If the direction to boil 20 minutes be followed,[4] these will both be broken down, and unless an excess of peroxide has been used, the difficulties mentioned by Mr. Hou,[5] are not likely in the chairman's opinion, to be met with. Please test Mr. Hou's suggestion, p. 373, cooling

[3] Page 133, JOURNAL, March, 1921.

[4] This should have read "these will in general both be broken down."

[5] JOURNAL, 1920, p. 367

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and making up to 500 cc. then filter off 200 cc., one hundred to be titrated as directed in the method, and one slowly evaporated to about 15 cc. and then diluted to 100 and titrated.

Please try the following method for acid, which is known to give low results. Place 20 grams of leather in an Erlenmeyer with 200 cc. of neutral 95 per cent alcohol. Shake frequently and allow to stand over night. Withdraw 100 cc. and titrate with tenth normal alkali and phenolphthalein.

Please make suggestions in regard to other possible methods for free acid. Please send in your report by May 5th.

The chairman was in fault in sending out directions to test Leather A for mineral acid by the alcohol extraction method. He had not tried it, and was unaware that this leather contained as part of its stuffing a considerable amount of free fatty acid, which dissolves more or less completely in the alcohol and is titrated.

Results of the collaborative work follow:

Leather A

	Cr_2O_3 by fusion with borax and carbonates	First ppt'g with NH_3	Fusion with Na_2O_2	Hou modification	H_2O
L. A. Cuthbert	3.43		3.44	3.41	9.00
R. W. Frey	2.97	2.90	2.42	2.42	9.66
E. L. Wallace	3.26		1.78	1.78	9.02
L. Balderston	3.34		2.62	2.61	9.45

Mr. E. L. Wallace also used the method suggested by Procter, of fusion or rather sintering, with MgO and Na_2CO_3, getting 3.27 per cent Cr_2O_3.

Leather B

	Cr_2O_3 by fusion with borax and carbonates	First ppt'g with NH_3	Fusion with Na_2O_2	Hou modification	H_2O	H_2SO_4
L. A. Cuthbert	4.67		4.59	4.58	8.91	0.05
R. W. Frey	4.65	4.58	4.65	4.65	9.71	0.17
E. L. Wallace	4.69		4.67	4.67	9.07	0.20
L. Balderston	4.53		4.54	4.52	9.40	0.19

COMMENTS OF COLLABORATORS

L. A. CUTHBERT, Elk Tanning Co. Laboratory, Ridgway, Pa. The residue left on the filter after the first fusion of Leather A, method *a* had a yellowish tinge and gave an appreciable amount of chromate on second fusion. I believe a second fusion is necessary in the case of leathers such as A.

Leather A, method *b* requires at least two fusions. Unless one is familiar with the leather with which he is working, a serious error may result with leathers of this kind which had received but one fusion.

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If the fused mass after fusion with Na_2O_2 be boiled 20 to 25 minutes, from my results I should say that it is unnecessary to evaporate the solution down to 15 cc. as suggested by Mr. Hou.

Color changes with starch indicator were correct in nearly all cases. With one or two exceptions, the blue color did not return after standing half an hour.

R. W. FREY, Leather and Paper Laboratory, Bureau of Chemistry: It will be noted that the results for Leather A show a decided discrepancy by the two methods. It seems strange that the Na_2O_2 fusion gives the lower results, for it would certainly seem the more powerful oxidizing agent.

E. L. WALLACE, Bureau of Standards: Sample A, method *a*. After dissolving the melt in hot dilute HCl, it was found necessary to make a second fusion on the residue, (consisting mostly of $BaSO_4$) in order to obtain all the chromium in solution. Method *b* was found to give much lower results than the other method, due to the formation of insoluble $BaCrO_4$. The residue after filtering as directed was treated with dilute H_2SO_4 and a large amount of chromic acid was liberated. It is evident from these results that the Na_2O_2 method cannot be relied upon in the analysis of leathers containing barium.

Mr. Cuthbert was the only one of the collaborators to make a second fusion in the case of Leather A, method *b*. The method as given calls for no second fusion, but his results indicate that by this means the two methods can be brought into concordance even in extreme cases.

Excepting in the case of leathers containing barium, a second fusion is almost never necessary with method *a*, and the chairman is inclined to believe that the peroxide fusion method ought to be dropped, as it saves but little time under any circumstances.

LABORATORY OF J. E. RHOADS AND SONS, WILMINGTON, DEL.

DETERMINATION OF OIL AND GREASE IN LEATHER—1922 COMMITTEE REPORT

W. K. Alsop, Chairman

The following letter was sent to members of the Committee:

"The Council of the A. L. C. A. has asked me to act as Chairman of this Committee. It is my understanding of their wishes in this matter that we review the work done, conduct further

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experimental work if necessary, but if possible to recommend a method that will be satisfactory for adoption by the Association.

The report of the Committee for 1919, J. A. Wilson, Chairman,[1] gives the result of a large amount of experimental work and the majority of the Committee favored the adoption of chloroform as the official solvent to replace petroleum ether.

Two reports on this subject by the Committee on Dressing Leather Analysis of the S. L. T. C. are given in their Journal.[2] Either chloroform or benzene is recommended for the official solvent.

The report of the A. L. C. A. Committee for 1921, F. P. Veitch, Chairman,[3] contains a good resumé of the work done heretofore and Mr. Veitch also recommends chloroform as the official solvent.

In the report of the 1921 Committee on Sampling of Leather, F. H. Small, Chairman,[4] are given results of some extractions with petroleum ether followed by chloroform.

In spite of the recommendations made by Committees studying this matter there is considerable sentiment in the Association against the adoption of chloroform as the official solvent in place of petroleum ether. It has been demonstrated that chloroform extracts more material in most or all cases from the leather and in many cases more grease and oil.

It is also clear that in most cases at least the chloroform extracts something else besides the grease or oil. In so far as I know, no attempt has been made by the Committees to determine whether in some instances the error introduced in this way may not be in excess of that occasioned by the use of petroleum ether. It evidently is so with the leather and the conditions described in the JOURNAL, August, 1921, page 400.

I do not understand that it is the desire of the Council that this Committee make further search for some solvent not yet tried, but mainly to settle the question as between petroleum ether and chloroform, the latter being preferred as the result of the large amount of experimental work done so far with various solvents.

[1] This JOURNAL, Vol. 14, pages 140–178.
[2] Jan., 1920, page 7, and December 1920, page 300.
[3] JOURNAL, September, 1921, pages 458–473.
[4] JOURNAL, August, pages 399 and 400.

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It seems to me that one factor the Committees working on this matter have not taken into consideration is the fact that apparently chloroform is not a reliable solvent for oils and grease if *water is present* and that experiments should be made to settle this. If this is the case, we will have to devise some method taking this into consideration if it seems advisable to use chloroform, or possibly both petroleum ether and chloroform for extraction."

Replies were received from them and after considerable delay two samples of sole leather and a sample of belting leather were sent out.

The directions for experiments designed to elucidate some features which had not been given consideration by previous Committees follow:—

A. Determine moisture content in 10 grs. of each sample by drying 2 hours at 105° C. in a hot air oven.

B-1. Extract 10 grams of each sample of the *original* leather with chloroform for 6 hours. Determine percentage of extract.

B-2. Re-extract samples from B-1 with chloroform for 6 hours more. Determine percentage of extract.

B-3. Extract 2 samples of each of the *original* leathers with petroleum ether for 6 hours. Determine percentage of extract.

B-4. Re-extract samples from B-3 with petroleum ether for 6 hours. Determine percentage of extract.

B-5. Re-extract 1 sample of each leather from B-4 with chloroform for 6 hours. Determine percentage of extract.

B-6. Re-extract 1 sample of each leather from B-4 with chloroform for 6 hours, previously drying the leather 2 hours at 105° C. to eliminate moisture. Determine percentage of extract.

C. Weigh 10 grams of each sample in crystallizing dishes and place in desiccators from which the dehydrating material has been removed and replaced by water. Weigh samples at the end of 48 hours to determine increased water content and extract at once with chloroform as in B-1 and B-2.

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TABLE I.—LEATHER NO. 1. PERCENTAGE OF EXTRACT ON BASIS OF ORIGINAL LEATHER

	A Moisture	B-1	B-2	B-1 + B-2	B-3	B-4	B-3 + B-4	B-5	B-6	B-3 + B-4 + B-5	B-3 + B-4 + B-6	C-1	C-2	C-3	C-2 + C-3
I. D. Clarke	10.70	5.26	.29	5.55	4.36	.02	4.38	.99	.31	5.37	4.69	1.245	5.59	.22	5.81
L. A. Cuthbert	11.75	4.93	.15	5.08	4.41	.03	4.44	.39	.30	4.83	4.74	.896	5.43	.22	5.65
G. V. Downing	11.35	4.25	.86	5.11	4.52	.05	4.57	.56	.38	5.13	4.95	.528	4.99	.55	5.54
J. S. Downing	10.30	5.49	.45	5.94	4.95	.16	5.11	1.47	.26	6.58	5.37	1.286			5.72
J. J. Meehan	11.60	5.06	.18	5.24	4.59	.01	4.60	.89	.27	5.49	4.87	.792	5.29	.29	5.58
G. W. Schultz					4.38	*.24	4.62	.79	.42	5.41	5.04				
L. E. Stacy and L. N. Nelson	12.35	5.50	.17	5.67	4.48	.05	4.53	.60	.24	5.13	4.77	1.227	5.70	.16	5.86
L. Balderston	9.95	5.01	.20	5.21	4.48	.05	4.53	.40	.27	4.93	4.80	1.526			5.55
Average	11.14	5.07	.33	5.40	4.52	.08	4.60	.76	.30	5.36	4.90	1.071	5.40	.29	5.67

* 16 hours extraction.

B-1 = 6 hours extraction with chloroform.
B-2 = 6 hours re-extraction with chloroform.
B-1 + B-2 = Total of 12 hours extraction with chloroform.
B-3 = 6 hours extraction with petroleum ether.
B-4 = 6 hours re-extraction with petroleum ether.
B-3 + B-4 = Total of 12 hours extraction with petroleum ether.
B-5 = 6 hours re-extraction of leather from B-4 with chloroform.
B-6 = 6 hours re-extraction of leather from B-4 with chloroform drying leather 2 hours at 105° C. before chloroform extraction.
B-3 + B-4 + B-5 = 12 hours extraction with petroleum ether and 6 hours with chloroform.
B-3 + B-4 + B-6 = 12 hours extraction with petroleum ether and 6 hours with chloroform drying leather 2 hours at 105° C. before chloroform extraction.
C-1 = Gain in weight of 10 grs. leather after 48 hours in desiccator with water.
C-2 = C-1 extracted 6 hours with chloroform.
C-3 = Re-extracted 6 hours with chloroform.
C-2 + C-3 = Total of 12 hours extraction with chloroform.

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TABLE II.—LEATHER NO. 2 PERCENTAGE OF EXTRACT ON BASIS OF ORIGINAL LEATHER

	A moisture	B-1	B-2	B-1 + B-2	B-3	B-4	B-3 + B-4	B-5	B-6	B-3 + B-4 + B-5	B-3 + B-1 + B-6	C-1	C-2	C-3	C-2 + C-3
I. D. Clarke	10.68	6.25	.37	6.62	5.26	.01	5.27	1.24	.26	6.51	5.53	.937	6.50	.33	6.83
L. A. Cuthbert	11.75	5.99	.16	6.15	5.27	.02	5.29	.37	.26	5.66	5.55	.490	6.47	.23	6.70
G. V. Downing	11.36	6.09	.27	6.36	5.48	.10	5.58	.60	.44	6.18	6.02	.226	6.62	.27	6.89
J. S. Downing	10.30	6.81	.35	7.15	5.35	.16	5.51	.67	.32	6.18	5.83	1.075			6.91
J. J. Meehan	11.60	6.16	.19	6.35	5.33	.03	5.36	1.01	.36	6.37	5.72	.539	6.52	.26	6.78
G. W. Schultz					5.36	*.29	5.65	.70	.35	6.35	6.00				
L. E. Stacy and L. N. Nelson	12.34	6.48	.36	6.84	5.30	.05	5.35	.38	.34	5.73	5.69	.919	6.52	.22	6.74
L. Balderston	11.45	6.10	.13	6.23	5.42	.02	5.44	.50	.23	5.94	5.67	1.134			6.77
Average	11.35	6.27	.26	6.53	5.35	.09	5.43	.68	.32	6.11	5.75	.760	6.53	.26	6.80

* 16 hours extraction.

B-1 = 6 hours extraction with chloroform.
B-2 = 6 hours re-extraction with chloroform.
B-1 + B-2 = Total of 12 hours extraction with chloro form.
B-3 = 6 hours extraction with petroleum ether.
B-4 = 6 hours re-extraction with petroleum ether.
B-3 + B-4 = Total of 12 hours extraction with petroleum ether.
B-5 = 6 hours re-extraction of leather from B-4 with chloroform.
B-6 = 6 hours re-extraction of leather from B-4 with chloroform drying leather 2 hours at 105° C. before chloroform extraction.
B-3 + B-4 + B-5 = 12 hours extraction with petroleum ether and 6 hours with chloroform.
B-3 + B-4 + B-6 = 12 hours extraction with petroleum ether and 6 hours with chloroform drying leather 2 hours at 105° C. before chloroform extraction.
C-1 = Gain in weight of 10 grs. leather after 48 hours in desiccator with water.
C-2 = C-1 extracted 6 hours with chloroform.
C-3 = Re-extracted 6 hours with chloroform.
C-2 + C-3 = Total of 12 hours extraction with chloroform.

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TABLE III.—LEATHER NO. 3. PERCENTAGE OF EXTRACT ON BASIS OF ORIGINAL LEATHER

	A Moisture	B-1	B-2	B-1 + B-2	B-3	B-4	B-3 + B-4	B-5	B-6	B-3 + B-4 + B-5	B-3 + B-4 + B-6	C-1	C-2	C-3	C-2 + C-3
I. D. Clarke	7.33	17.94	.12	18.06	16.48	.02	16.50	1.81	.98	18.31	17.48	.994	18.68	.10	18.78
L. A. Cuthbert	8.05	17.80	.20	18.00	16.40	.03	16.43	1.10	.76	17.53	17.19	.735	18.53	.10	18.63
G. V. Downing	6.51	17.85	.67	18.52	16.70	.14	16.84	1.30	.26	18.14	17.10	.905	18.99	.22	19.21
J. S. Downing	7.15	18.51	.22	18.73	‡17.16	‡.95		1.37	.82			1.048			19.11
J. J. Meehan	7.73	18.28	.18	18.46	16.70	.00	16.70	1.69	1.00	18.39	17.70	.866	18.60	.15	18.75
G. W. Schultz					16.56	*.29	16.85	1.58	1.12	18.43	17.97				
L. E. Stacy and L. N. Nelson	8.06	18.21	.35	18.56	16.76	.05	16.81	1.17	.90	17.98	17.71	1.038	18.55	.20	18.75
L. Balderston	8.06	17.95	.34	18.29	16.52	.03	16.55	.70	.69	17.25	17.24	1.125			19.32
Average	7.56	18.08	.30	18.37	16.59	.08	16.67	1.34	.81	18.00	17.48	.959	18.67	.15	18.94

‡ Omitted from average on account of B-4.
* 16 hours extraction.

B-1 = 6 hours extraction with chloroform.
B-2 = 6 hours re-extraction with chloroform.
B-1 + B-2 = Total of 12 hours extraction with chloroform.
B-3 = 6 hours extraction with petroleum ether.
B-4 = 6 hours re-extraction with petroleum ether.
B-3 + B-4 = Total of 12 hours extraction with petroleum ether.
B-5 = 6 hours re-extraction of leather from B-4 with chloroform.
B-6 = 6 hours re-extraction of leather from B-4 with chloroform drying leather 2 hours at 105° C. before chloroform extraction.
B-3 + B-4 + B-5 = 12 hours extraction with petroleum ether and 6 hours with chloroform.
B-3 + B-4 + B-6 = 12 hours extraction with petroleum ether and 6 hours with chloroform drying leather 2 hours at 105° C. before chloroform extraction.
C-1 = Gain in weight of 10 grs. leather after 48 hours in desiccator with water.
C-2 = C-1 extracted 6 hours with chloroform.
C-3 = Re-extracted 6 hours with chloroform.
C-2 + C-3 = Total of 12 hours extraction with chloroform.

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The petroleum ether used should all boil below 80° C. The chloroform should be redistilled.

The following members collaborated in this work:

Lloyd Balderston, J. E. Rhoads & Son., Wilmington, Del.

I. D. Clarke, Leather & Paper Laboratory, Bureau of Chemistry, Washington, D. C.

J. S. Downing, Bona Allen, Inc., Buford, Georgia.

L. M. Whitmore and G. V. Downing, Leas & McVitty, Inc., Salem, Va.

J. J. Meehan, Graton & Knight Mfg. Co., Worcester, Mass.

L. E. Stacy and L. N. Nelson, C. C. Smoot & Sons Co., North Wilkesboro, N. C.

L. A. Cuthbert, Elk Tanning Co., Ridgway, Pa.

G. W. Schultz, Elk Tanning Co., Ridgway, Pa.

The results reported are shown in tables No. 1, 2, and 3.

The comments of those reporting are as follows:—

LLOYD BALDERSTON: I think it sufficiently evident that chloroform should not replace petroleum ether as the principal solvent, because it removes matter which is not grease nor wax, and because the amount it extracts depends on the moisture content of the sample.

I believe petroleum ether should be retained as the first solvent to be used in grease extraction, and that where a more complete examination is needed it should be followed by carbon tetrachloride, sulphuric ether or chloroform, or two of these.

Committee work should be done on leathers stuffed with various known mixtures of oils, sulphonated oils, hard greases, soaps, waxes, wool grease, oxidized oils, and any other materials which are used for stuffing leather, and a series of solvents agreed upon, with the order in which they are to be used.

I. D. CLARKE: The extractions were first carried out in a Johnson apparatus and then repeated in a soxhlet extractor. In the Johnson apparatus the vapor from the boiling solvent completely surrounds the leather and the temperature of the latter is therefore slightly higher than it is in a soxhlet apparatus. With petroleum ether there was practically no difference, but with chloroform more extract was always obtained with the Johnson extractor. The soxhlet siphoned between two and three times an hour. More extract was obtained in every case with chloro-

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TABLE IV. I. D. CLARKE—DETERMINATION OF OIL AND GREASE IN LEATHER

		Johnson extractor						Soxhlet extractor					
		Sample No 1	Color of extract	Sample No. 2	Color of extract	Sample No. 3	Color of extract	Sample No. 1	Color of extract	Sample No. 2	Color of extract	Sample No. 3	Color of extract
A[1]	Moisture	10.61		11.42		7.50							
A[2]	Moisture	11.05		11.44		7.31							
A[3]	Moisture	10.37		10.99		7.17							
B1	Extd. 6 hrs. with chloroform	5.26	d.r.s.&l.b.liq.	6.25	d.r.s.&l.b.liq.	17.94	d.b.s.	4.56[5]	l.b. liq.	5.97	d.r.s.&l.b.liq	17.64	b.s.
B2	B1 cont. 6 hrs. with chloroform	0.29	y.b.	0.37	r.b.	0.12	y.b.	0.34	b.s.	0.15	b.s.	0.25	b.s.
B2[4]	B2 cont. 6 hrs. with chloroform	0.19	r.b.	0.25	r. & b.s.	0.08	b.y.s.	0.04		0.06	l.b.	0.06	b.
B3	Extd. 6 hrs. with petroleum ether	4.33	l.y. liq.	5.30	l.y. liq.	16.45	l.b.s.	4.36	l.y. liq.	5.13	l.y.	16.54	l.b.y.s.
B3	Extd. 6 hrs. with petroleum ether	4.40	l.y. liq.	5.22	l.y. liq.	16.52		4.27	l.y. liq.	5.14	l.y.	16.17	l.b.y.s.
B4	B3 cont. 6 hrs. with petroleum ether	0.02	l.y.	0.01	l.y.	0.02	l.y.	0.05	l.y.	0.03	l.b.	0.06	l.b.
B4	B3 cont. 6 hrs. with petroleum ether	0.01		0.01	l.y.	0.02	l.y.	0.03	l.y.	0.03	l.b.	0.06	l.b.
B5	B4 extd. 6 hrs. with chloroform	0.99	b.s.	1.24	b.s.	1.81	b.s.	0.34	b.s.	0.77	b.s.	1.39	b.s.
B6	B4 extd. 6 hrs. with chloroform after drying at 105°	0.31	l.b.s.	0.26	l.b.	0.98	b.s.	0.20	b.s.	0.18	l.b.s.	0.71	b. s.
C1	Increase in weight	1.2446		0.9371		0.9943							
C2	C1 extd. 6 hrs. with chloroform	5.59	d.r.s.&y.b.liq.	6.50	d.r.s.&y.b.liq.	18.68	r.b.s.						
C3	C2 contd. 6 hrs. with chloroform	0.22	v.l.y.	0.33	r.b.s.&b. liq.	0.10	l.y.						
D1	Increase in weight	1.3166		0.8126		0.9665							
D2	D1 extd. 6 hrs. with petroleum ether.	3.65	l.y. oil	4.78	l.y. oil	16.97	l.r.y.s.						
D3	D2 cont. 6 hrs. with petroleum ether	0.51		0.43		0.01							
B1 and B2		5.55		6.62		18.06		4.90		6.12		17.89	
B3 and B4		4.38		5.27		16.50		4.35		5.16		16.41	
B3, B4 and B5		5.37		6.51		18.31		4.69		5.93		17.80	
B3, B4 and B6		4.69		5.53		17.48		4.55		5.34		17.12	

(All results are expressed as percentages of original leather unless otherwise indicated).

[1] Moisture on 10 gms. of leather dried 2 hrs. at 105° in tannin dishes, April 11.
[2] Moisture on 5 gms. of leather dried 2 hrs. at 105° in weighing bottles, April 13.
[3] Moisture on 5 gms. of leather dried 2 hrs. at 105° in weighing bottles, April 24.
[4] Extraction continued 6 hrs. after first two 6-hour extractions.
[5] Boiled slower than others.
[6] Abbreviations used: d.—dark; r.—red; s.—solid; l.—light; b.—brown; liq.—liquid; y.—yellow; v.—very.

C1 Gain in weight in grams after 48 hours in a desiccator containing water.
C2 Percentage extract obtained in 6 hrs. with chloroform and leather from C1.
C3 Percentage extract obtained by re-extracting samples from C2 for 6 hrs. with chloroform.
D1 Gain in weight in grams after 48 hours. in a dessicator containing water.
D2 Percentage extract obtained in 6 hrs. with petroleum ether and leather from D1.
D3 Percentage extract obtained by re-extracting samples from D2 for 6 hrs. with petroleum ether.

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form than with petroleum ether. Some of the chloroform residues were treated with warm water and the water extracts tested with gelatine-salt solution and with iron alum solution. No precipitate could be detected with gelatine-salt and there was only a slight blue coloration with iron alum. Drying the leather caused an appreciable decrease in the amount of material extracted by chloroform and if the sum of B-3, B-4 and B-6 can be considered as the correct value then for these samples the positive error with chloroform due to moisture is greater than the negative error with petroleum ether.

The addition of more water or moisture to the leather increased the amount of extract obtained with chloroform during the first 6 hours. The addition of moisture decreased the rate at which the fat was extracted by petroleum ether from samples No 1 and No. 2 but in 12 hours the quantity of fat extracted was nearly the same as that extracted from samples without the additional moisture. From sample No. 3, however, more extract was obtained when the moisture was increased and in some cases therefore there may be a considerable error due to moisture not only with chloroform but also with petroleum ether.

Mr. Clarke submitted a complete tabulation of his results which are inserted as Table No. 4.

G. V. DOWNING: It seems quite probable that chloroform removes a small amount of tanning material. It also removes more of the oxidized oils and fats than does petroleum ether. The moisture content has more influence on the chloroform extract than upon the petroleum ether extract.

The use of chloroform as a solvent depends upon the definition of extractable oils and greases. There is always the question of how much grease should be called extractable. In the case of leathers completely tanned with oil the extractable oils should hardly include the oxidized ones. In the case of sole leather oiled with a large percentage of oxidizable oils the chloroform extraction will be higher than that from petroleum ether, and will contain some of these oxidized oils which might be considered as leather.

If chloroform were adopted, we would recommend that the leather be dried over calcium chloride to bring to as nearly an anhydrous state as possible.

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J. S. DOWNING: From the results it would appear that the presence of moisture has a considerable effect on the extracted matter. It is my opinion that the preferable procedure is to extract the leather first with petroleum ether, then dry it and continue the extraction with chloroform.

J. J. MEEHAN: "The results obtained by this Committee work clearly show that the presence of moisture has a decided effect on the amount of material extracted by chloroform. The per cent of residue in each case is larger than that obtained with the use of petroleum ether, but the appearance of the residue does not warrant the conclusion that it consists entirely of grease. Nothing was done to determine the actual percentage of fatty matter present in the residue, but from previous work done by yourself and J. S. Downing, I believe it is safe to assume that at the utmost only 50 per cent of the residue extracted with chloroform, subsequent to the petroleum ether extraction, would be fatty matter.

If we assume that the material extracted in B-5 is largely foreign matter and deduct this percentage from the respective figure obtained in B-1, we have a result which approximates that found in B-3, so that it may be reasonable to suppose that the grease figure found in B-3 is more nearly correct than the larger amount found in B-1.

Again in C experiment, residues obtained show an average increase for each sample of 0.52 per cent when compared with the figures in B-1, and this added ½ per cent surely cannot be grease. As stated above, the appearance of the chloroform extracts differed considerably from that of the petroleum ether extracts, and possibly if the extraction had been carried on for another 6 hours, 0.2 or 0.3 per cent more residue might have been obtained in each case, as the end of the extraction does not seem to be definite, varying as it does with the moisture content of the leather.

The petroleum ether extraction appears to be reasonably constant and presumably contains nothing but grease, and to this extent at least petroleum ether would seem to be a better solvent than chloroform. If the added material removed from the leather by chloroform is not all grease and previous work having made this assumption reasonable, then a considerable error appears in all grease extraction work done with chloroform, this error being increased or lessened in accordance with the percentage of water

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present in the leather. Even if we start with an absolutely dry leather we have no assurance at the present time that at the end of the extraction a product composed entirely of grease has been obtained.

For the above reasons I believe that more work should be done on this subject before chloroform is selected as the official solvent.

L. E. STACY AND S. N. NELSON: The six hour extraction with petroleum ether seems to extract all the oil and grease. An examination of the residues from B-5 show them to be a gummy mass consisting mostly of organic coloring matter, with none of the characteristic properties of oil and grease. The amount of this organic residue varies with the different tannages of leather.

Time not permitting an analysis to determine the composition of the three leathers submitted it is hard to compare, or to draw conclusions from the results obtained, though a study of these results brings out some interesting data.

The sum total of the petroleum ether extracts is lower by 1.13—1.49 and 1.74 per cent respectively than the total chloroform extractions. And when the chloroform extracts of B-5 are added to the petroleum ether extracts of B-3 and B-4 the percentages still fall short from approximately 0.5 to 1.1 per cent of the total amount extracted by chloroform. This is strikingly noticable in case of leather No. 2—the difference amounting to 1.1 per cent. The residue from B-5 represents only 0.39 per cent and it is hardly reasonable to assume that the residue from an additional 6 hour chloroform extraction would amount to 1.1 per cent of the original leather. But in case of leather Nos. 1 and 3 the above assumption will not hold true.

The wide variation in the percentages of the residues from the chloroform extractions after a 12 hour extraction by petroleum ether is due no doubt to the character of the coloring matter extracted by chloroform. We are of the opinion that the composition of the leather is a determining factor in the amount of coloring matter extracted.

We fail to see any advantage in adopting a method that gives in addition, to the oils and greases, a small per cent of coloring matter. We, therefore, recommend that the Association retain its present Official Method for the determination of oil and greases in leather.

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TABLE V.—AVERAGE PERCENTAGE OF EXTRACT. COMPILED FROM TABLES I, II AND III

	B-1 + B-2 Chloroform total of two 6 hour extractions	B-3 + B-4 Pet. ether total of two 6-hour extractions	B-3, B-4 and B-5 Pet. ether 12 hours chloroform 6 hours	B-3, B-4 and B-6 Pet. ether 12 hrs. Then leather dried extracted 6 hours with chloroform	C-2 + C-3 Leather 48 hrs. in desiccator with water present. Extracted two 6-hour periods with chloroform
Leather No. 1	5.49	4.60	5.36	4.90	5.67
Leather No. 2	6.53	5.43	6.11	5.75	6.80
Leather No. 3	18.37	16.67	18.00	17.48	18.94

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The results from collaborators vary considerably in some particulars but they all seem to point to certain things that are shown in Table No. 5 which is comprised of average results.

Consideration of these average results ranging them from the highest to the lowest show:

1. The highest results by extraction with chloroform of leather containing the most water.
2. Extraction with chloroform of leather containing about the normal amount of water.
3. Extraction with petroleum ether followed by chloroform.
4. Extraction with petroleum ether, the leather then dried and re-extracted with chloroform.
5. The lowest results by extraction with petroleum ether,

The difference in results by the various methods of extraction may best be shown as follows:

	1	2	3
Leather No. 1	0.80	0.30	0.50
Leather No. 2	1.10	0.32	0.78
Leather No. 3	1.70	0.81	0.89

NOTE:—1 is per cent extracted by chloroform from the original leather in excess of the amount by petroleum ether.
2 is per cent extracted by chloroform after extraction of the original leather by petroleum ether. The leather being dried before the chloroform extraction.
3 is difference between No. 1 and No. 2.

The results in column 2 represent all that was extracted by chloroform from the leather which had been previously extracted with petroleum ether and then had the water eliminated and should contain all the grease or oil extractable by chloroform in excess of petroleum ether. If this is true then, as shown in column 3, the amount of material, other than oil or grease, extracted from the original leather by chloroform is in excess of the fats or oil. *Further, all of the extract represented in column 2 is not grease or oil.*

There has not been time to submit the tabulated results to the members of the committee but it is evident from the results and comments that the committee is not in favor of substituting chloroform for petroleum ether as the solvent for use in our official method and therefore it is recommended that the Association retain its present method. It is also recommended that the com-

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mittee be continued and further work done along the lines suggested by members, possibly involving the use of two or more extractions and solvents as noted by Dr. Balderston.

Personally, I do not consider chloroform a satisfactory solvent under the conditions and think that the proposal to use it instead of petroleum ether may as well be put to sleep. Also that the fact that chloroform extracts more material from the leather is no great argument for its use, in view of the fact that other materials not related at all to oils and grease are extracted.

One of the members wrote me as follows:

"Oils that are applied to the leather, and subsequently become oxidized or otherwise made insoluble in the ordinary fat solvent, are as much combined as any other material deposited on the fibres. The fact that they were once oils is no reason for trying to determine them as oils. There would be as much reason in adapting a solvent (say NaOH) that would extract the greatest amount of 'water soluble materials.'

I hope that further search for a method will not bring about conditions paralleling our method for 'Water Solubles' in leather. Perhaps we need a definition for oil and grease in leather (or out of it)."

ABSTRACTS

Gambier Cutch. *Bull. Soc. Ind. Mulhouse*; 279, (1921), through *Col. Tr. Jour.*, **10,** 117. When Gambier extract is employed in the silk weighting there is usually considerable loss due to the presence of impurities in the product, and also to the fact that catechin possesses but a slight attraction for silk weighted with tin. It was thought that pure Indragiri Gambier would be better than the Chinese product but in actual use is proved to be of less value and manufacturers refused to use it. Catechin may be readily isolated from the catechutannic acid in Indragiri Gambier, and it was found that while the latter acid possesses a great attraction for silk weighted with tin, catechin itself not only has no weighting action, but actually removes some of the tin weighting to the extent of three per cent. Pure hematoxylin shows a similar behavior when compared with Campeachy wood extract. On the other hand, when a bath of Gambier extract or catechin is used for a second time in weighting silk, there is a considerable increase in the weight, due to the fact that catechin undergoes some conversion when heated in the presence of air. Catechutannic acid behaves in an opposite manner, for after heating in the presence of air it is found to possess less weighting action.

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When pure Gambier extract is boiled for several hours in the presence of air, a clear extract is obtained, which no longer deposits catechin on standing, and can be preserved unaltered for years. During this process the catechin acts apparently with the catechutannic acid in some unknown manner to produce a combination suitable for the weighting of silk.

Manufacture and Properties of Fish Glue. By D. K. TRESSLER. *Chem. Age* (N. Y.), **29**, 173-5 (1921); through *C. A.*, **15**, 2366 (1921). Fish glue is made from waste products of fish. These products are divided into (1) heads, (2) trimmings and bones, and (3) skin from dried salt fish. After the salt has been washed out, (2) and (3) are extracted with hot water until the liquor contains about 5 per cent glue. This is drawn off and the extraction repeated. A preservative is added and the glue liquor is evaporated to 50-55 per cent solids. An essential oil is added to mask the odor. The heads are bleached and extracted with dilute acid. The residue, "*Chum*," contains approximately 50 per cent protein and is sold as *chicken-feed* or as *fertilizer*. The glue is usually marketed as liquid glue since it is soluble in water at ordinary temperatures. The grades are (1) photo-engraving glue from first-run liquor from the skins, (2) fish-waste glue, and (3) fish-head glue. They should have a gel point of about 7.5, should not contain more than 0.2 per cent NaCl, and should not be sticky or liquid when an eighth inch layer is dried at 25° with 80 per cent humidity. Fish glues consist chiefly of proteoses and peptones with some proteins and resemble bone glues more than hide glues. Much fish glue contains a white pigment since alone it forms a dark glue line. When properly preserved it will keep indefinitely. It is used in *photo-engraving*, and wherever flexible glue is required.

Chrome Tanning VIII. A New Method for the Determination of the Basicity Figures of Chrome Liquors, Part I. BY D. BURTON, A. GLOVER AND R. P. WOOD. *J. S. L. T. C.*, **6**, 92 (1922). Determinations for acidity on pure chrome solutions were carried out as follows:—Fifty cc. of the solution was pipetted into a conical flask and 25 cc. of "20 volume" H_2O_2 added. Twenty-five to thirty cc. of N/1 NaOH was added. After diluting with about 50 cc. distilled water a funnel was placed in the flask to prevent loss by spurting and the solution heated up gently and then boiled for half an hour. The inside and outside of the funnel were rinsed with distilled water into the flask, 25-30 cc. N/1 H_2SO_4 added and the solution brought to the boil again. It was then diluted with cold freshly-boiled distilled water (CO_2-free and renders the end-point much more definite) and titrated with N/1 NaOH, five drops of a 1 per cent solution of phenolphthalein in acetone being added when the clear lemon yellow color appeared. The addition of alkali was then continued until the color changed to a reddish hue, which was definite to within one drop of alkali. The solution was then cooled, acidified with 10 cc. pure concentrated HCl, cooled again and made up to 500 cc. Fifty cc. was pipetted into a flask, 15 cc. concentrated HCl

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added, the liquid cooled and 10 cc. of a 10 per cent solution of KI added. After allowing to stand from seven to ten minutes the solution was titrated with N/10 $Na_2S_2O_3$ using starch as indicator.

In order to ensure as great a degree of accuracy as possible the acidity of the H_2O_2 was determined by adding excess of N/10 NaOH, bringing to the boil and titrating back the excess with N/10 H_2SO_4 using phenolphthalein (dissolved in acetone) as indicator. By substracting one-tenth of this and two-thirds of the $Na_2S_2O_3$ reading from the amount of alkali required the acidity is given in cc. N/1 H_2SO_4.

The results obtained seem to warrant the conclusion that the method is capable of yielding concordant results for the acidity of pure solutions.

Relative Adsorption From Liquors Prepared With Different Tanning Materials, Part I. By H. G. Bennett and N. L. Holmes. *J. S. L. T. C.*, **6**, 49 (1922). Empirical adsorption isotherms have been determined for three types of myrobalans, for mimosa bark and for the several parts of valonea. The procedure consisted of shaking 110 cc. of the aqueous extract of these materials in a series of increasing concentrations with 1 gram of specially prepared hide powder. After shaking for 30 minutes the solutions were filtered and the final concentration determined from the total solids in an aliquot. Graphs of the results show that myrobalans give a distinctly better adsorption than mimosa bark or valonea; that R_1 myrobalans give a better adsorption than J_1 or B_1 although it is doubtful whether these grades differ widely; that the liquor from valonea beard is of better weight-giving quality than that from whole valonea, while the acorn has very little value. The results show only an approximate agreement with the adsorption formula $x = mac^{1/n}$. Part II, *J. S. L. T C.*, **6**, 59 (1922). A continuation of the previous work on adsorption from infusions of the staple tanning materials. It is shown that adsorption is determined not merely by the equation $x = mac^{1/n}$, but that the "constant" a varies with the ratio of m to $(x + c)$. The authors consider that this is due to alterations in the specific surface of the adsorbents by a simultaneous adsorption of hydrions naturally present. It is concluded that in a blend of materials the adsorption may be better than either material alone, as the natural acidity of one material affects the adsorption of tan of the other material. It is concluded also that the mathematical expression of adsorption from tannin infusions is complex, especially in the case of mixtures, and is further complicated by the possibility of surface changes from other sources, such as lyotrope influence.

The Factor Relating the Density of a Solution to Its Concentration. By H. G. Bennett and N. L. Holmes. *J. S. L. T. C.*, **6**, 102 (1922). The factor (γ) connecting °Bkr of a solution with its concentration by volume, is shown to be determined in the case of inorganic salts by (1) the specific gravity of the solute, (2) the volume change it causes in dissolving, and (3) the position of its ions, especially the anion, in the lyotrope series.

It is suggested that the experimental determination of (γ) for solu-

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tions or crystals may be used to determine the density of the anhydrous solute, and also, in conjunction with its value for the solute (γ_0) to determine numerically (ψ) the lyotrope power of the substance under any conditions.

It is further pointed out that in the case of non-ionizable substances, and still more in the case of colloids, the value of (γ) is determined chiefly by the density of the solute, and is usually much more constant than for salts.

The values for γ of the soluble solids of tanning materials are found to be characteristic and to supply new criteria of quality. It is shown that in conjunction with M (non-tans per unit tan) rapid analyses may be made from hydrometer tests, which at worst are useful approximations. This idea is also utilized for rapid tintometer tests, for estimating weights to be taken for analysis, and for judging the density of an extract required.

The differing values of (γ) for bark and myrabs, are utilized to determine their proportion in mixture, to follow the course of leaching such blends, and to act generally as a criterion for technical control work.

It is suggested that the determination of the hydrophile index (ψ) and other physical-chemical data of tanning materials are hopeful lines of investigation.

Some Boot and Shoe Waxes and Finishes. By T. A. Smith. *J. S. L. T. C.*, **6**, 67 (1922). A general description of some of the materials used in boot and shoe manufacture is given. The materials mentioned are:— (1) Machine waxes made of resinous substances. (2) Bottom finishes similar to the ordinary pigment finishes. Stains. (3) Finishing waxes made by mixing melted true waxes with mineral waxes. (4) Upper leather dressings of the size and polish types.

It is proposed to give later, detailed accounts of differences in physical nature caused by the substitution of other ingredients for those usually employed in the composition of these materials.

The Swelling of Hide Powder, Part II. By E. C. Porter. *J. S. L. T. C.*, **6**, 83 (1922). A continuation of previous work [Abst., This Jour., **17**, 128 (1922)]. With the object of making a closer study of the swelling phenomena at or near the maxima for acid and alkaline swelling.

The Application of the Proctor-Searle Method to the Determination of the Acidity of Chrome Leather. By. W. R. Atkin. *J. S. L. T. C.*, **6**, 89 (1922). Experiments with chrome liquors in an attempt to correct for the alkali used up in forming sodium chromate when using the Procter-Searle method. The acidity of the liquors as found with a modification of the Procter-Searle method was higher in every case than that found by the Procter-McCandlish method. The cause of this difference has not yet been ascertained.

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The Clarification of Solutions Containing Reducing Sugars by Basic Lead Acetate. The Effect of Different Deleading Agents. By D. T. Englis and C. Y. Tsang. *J. A. C. S.*, 44, 865 (1922). A comparative study has been made of the effect of removal of basic lead acetate from solutions of glucose and fructose by means of potassium oxalate, disodium phosphate, potassium sulfate, potassium sodium tartrate and sodium carbonate. With glucose the quantity of sugar carried down by the lead precipitates, as indicated by loss in reducing power, varies from less than 1 per cent to as much as 10 per cent; with fructose, from less than 1 per cent to as much as 35 per cent. Disodium phosphate seems to be the most satisfactory deleading agent.

The loss of sugar appears to be caused primarily by occlusion in the lead precipitate, since on washing the precipitate a much smaller loss is observed.

Titration Curve of Gelatin. By D. J. Lloyd and C. Mayes. *Proc. Roy. Soc.*, B93, 69 (1922); through *J. S. C. I.*, 41, 224A (1922). Estimations were made of the hydrogen ion concentrations of solutions of gelatin in known concentrations of acid and alkali, and the amount of combined acid or alkali calculated in each case. It is concluded from the results that for concentrations of acid not exceeding 0.02N combination occurs at the free amino groups of the gelatin molecule; for greater concentrations of acid, however, there is probably also combination at the nitrogen of the peptide linkages. No conclusion was drawn as to the mode of attachment of alkalies, but it is probable that the number of positions of attachment for bases is different from the number of positions for acids, *i. e.*, that the reacting weight, molecular weight, basicity (or acidity), is not the same in acid and alkaline solution.

The Manufacture of Kid Leather. Anon. *Lea. Man.*, April (1922). Goatskins are received at the tannery in bales about four feet long by two feet wide and two and a half feet deep. The top and bottom are covered with burlap and they are bound with six or eight ropes. Such skins are known as drysalted, sun dried or arsenic cured. Some skins come wetsalted, in which case they are shipped in barrels. Nearly all raw goatskins are received at the tannery with the hair on.

The first operation is to soak the skins in paddle wheels containing water and usually some chemicals to aid in the softening. The softened skins are pulled from the paddle pits, grained and trimmed. The workmen throw a skin over a sloping beam, flesh side up and with a large butcher knife cut off the hard end of the shanks, ears, heads and any ragged edges which would not be likely to remain on the skin through the finishing operations. The trimmed skins are now washed in a pin wheel to thoroughly cleanse them of blood, dirt, etc., and then put into the limes. The liming is done in paddle pits in which the paddles are run occasionally to plunge up the limes and move the skins around so that they will be properly acted upon by the solution.

When limed to the proper degree so that the hair will slip readily the

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skins are removed from the lime paddles and unhaired on a serial table unhairing machine. This machine, consisting of several tables which pass between two sets of scraping rolls on which fine streams of water are always spraying, is operated by two men.

After unhairing the skins are next cleaned on the flesh side by a machine equipped with a scraper roll similar to the one on the unhairing machine only this roll carries spiral knives that are ground to sharp edge, while on the unhairing machine the edges are dull. Instead of serial tables the fleshing machine operates by having the skin thrown over a rubber roll, flesh side out, and the operator stepping his foot on a pedal which causes the roll to press the flesh side of the skin against the spiral knife roll and when the operator pulls the skin out of the machine the flesh is cut away so that the skin is clean and white on both sides.

The skins are now thick and in a condition somewhat like rubber and have to be delimed or bated before the actual tanning operations can be commenced. This is accomplished by running the skins in a paddle wheel containing a bacterial bate, usually, as the old manure bates have largely passed out of use in this country. Bating makes the skins soft and silky feeling and reduces the plump condition so that they are quite thin.

Pickling with sulphuric acid and salt immediately precedes the tanning and can be done in the same paddles in which the tanning is to be done. Many factories use the one bath chrome tannage for goatskins on account of its simplicity, economy and the generally satisfactory results obtained. The tanning is usually followed by a neutralizing bath of borax and water in a pin wheel.

The skins now are of a robin's egg blue color and feel firm and leathery and in fact are leather, and the remaining operations are mechanical or consist of the application of oils, dyes and finishes which are to control the appearance and feel of the finished product.

After neutralizing the skins are put out on a serial table machine to spread the skins out perfectly smooth, to work out the stretch, and to remove the excess liquids they contain so that they can be shaved.

Goatskins are of varying thicknesses and each skin also is much thicker in some parts than in others so nearly all have to be shaved to reduce the thickness of the heaviest and to make level. Shaving also cuts away the flesh fibers so that in all future operations the skin more readily responds to the stretching effect that nearly every operation has. This shaving is accomplished by applying the flesh side of the skin to a rapidly revolving roll carrying sharp blades.

After shaving, the skins are carefully sorted for weight and quality to determine what color they are to be dyed and what particular finishing order they are to be applied to.

The skins are now colored and fat-liquored in a pin wheel and set out to remove the excess of liquids contained and to make perfectly smooth. This completes the wet work on the skins and they leave the cellar and are taken to the top floor of the building, usually, where the finishing process commences.

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A coat of sperm oil is applied to the grain side by machine and the skins hung up in a warm room to dry. The application of oil keeps the grain soft and pliable so that the skins will not become cracked in handling, after they are dry. The dried skins are known as being in color crust and can be kept indefinitely in that condition before finishing. One peculiarity of goatskins is important enough to be noted at this time. Nearly all leathers are dried at this stage of the operations by tacking on boards, but in the case of goatskins a hard tinny leather would result, so they are never tacked, but dried over poles or hanging from the butt shanks. The various mechanical operations are relied upon to furnish all the straining that the skins require.

Any lot of skins desired to be finished are chosen from the color crust stock and dampened back for staking by packing in wet sawdust over night. Twelve or fifteen hours in the sawdust bring the skins to a dampened condition so that the fibers will stand the severe strain of the staking operations. The Slocumb type of staking machine is used and the skins are pulled in every direction, which stretches the fibers considerably. The skins are now dried to a nearly dry condition. The fibers will contract somewhat, so before they have become hard and firmly set the skins are staked again on the same type of machine and then hung up and thoroughly dried. This second staking while in a nearly dry condition again pulls the fibers apart just enough to insure the leather being soft and pliable and not stretchy nor hard and stiff.

The skins now receive a coat of seasoning, containing blood or albumen in some form, which makes it possible for the skins to take a bright glaze After this seasoning, which is done on a serial table machine, similar to a putting out machine, the skins are quickly dried on arm drier, like a clothes drier, trimmed with shears to remove any hard edges that would be likely to cause the skins to be pulled from the hands of the glazers, and then glazed on a sloping bed machine.

Sometimes a second or even third coat of seasoning is applied, and as many glazings follow, but more often a single application of seasoning and single operation of glazing is sufficient to produce the luster so characteristic of kid leather.

A final slicking up of the appearance of the leather is given by treatment with a hot steel roll, which has an ironing effect the same as though an ordinary flat iron was used.

Wool Scouring Wastes for Fertilizer Purposes. By F. P. Veitch. *Jour. Ind. Eng. Chem.*, 14, 434 (1922). This country uses more than 600,000,000 pounds of unscoured wool annually. Approximately half this weight consists of dirt, salts, grease, and albuminous and other organic matter which must be removed by careful washing. With the exception of the grease recovered at a few of the scouring plants, all of this material is wasted, being run into the streams of the country, seriously polluting the waters and rendering them unfit for domestic and many industrial purposes without purification at great expense.

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Analyses of a large number of samples of all grades of unscoured wool, both domestic and foreign, show that the grease content varies from 6 to 42 per cent, averaging 14 per cent; that the water-soluble matter varies from 6 to 33 per cent, averaging 14 per cent; that the nitrogen (other than that of the wool) varies from 0.3 to 1.1 per cent, averaging 0.6 per cent; and that the potash varies from 1 to 7 per cent, averaging 4 per cent.

Both the potash and the nitrogen compounds are water-soluble, and it is these and the other water-soluble constituents of wool that are of interest as fertilizer materials.

Under present conditions, the wool scouring plants of this country are wasting annually potash equivalent to approximately 100,000 tons of Kainit, worth at present quotations $840,000, and 42,000 tons of 4.5 per cent tankage, worth $280,000 to the fertilizer manufacturer.

Experiments have been conducted on a manufacturing scale in mixing concentrated wool scouring wastes with other waste materials for the purpose of determining the practicability of economically handling the material in the fertilizer factory. The material gave no trouble and the fertilizer manufacturer is ready to use the material as soon as it can be obtained in quantity, and, of course, at a price that will yield him a profit.

The work that has so far been done strongly indicates that wool scouring waste can be readily handled by the fertilizer manufacturer, giving him another source of potash, nitrogen, and filler of excellent quality, in an advantageous form. The farmer, the fertilizer manufacturer, the wool scourer, and the people and industries in the vicinity of wool scouring plants will benefit directly or indirectly from the recovery and utilization of the valuable but offensive and dangerous waste if it can be recovered economically.

Chrome Leather Analysis III. The Extraction of Oils and Fats from Chrome Leather. By D. Woodroffe. *J. S. L. T. C.*, **6**, 97 (1922). A brief review of recent work on the extraction of oils and fats from leather. A few preliminary experiments on the extraction of chrome leathers largely confirm previous work. Chloroform is considered the most efficient solvent for an impregnated chrome sole leather simply because the residue of the chloroform extract is greater than that of the other solvents used. On box calf fat liquored with sulphonated oil and glace kid fat liquored with soap and neatsfoot oil, benzene and trichlorethylene give greater residues than chloroform. The author points out that because of the higher boiling points of solvents such as benzene, trichlorethylene and carbon tetrachloride it will be necessary to heat the fat extract for sometime in order to expel all traces of these solvents and in consequence there will be more oxidation. Whether the increase in weight is sufficient to reject the use of the higher boiling solvents is a problem left for future investigation.

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The Evaluation of Gelatin and Glue. By R. H. Bogue. *Jour. Ind. Eng. Chem.*, 14, 435 (1922). The procedures in current use for the evaluation of gelatin and glue are based primarily upon the jelly consistency at low temperatures or the viscosity at high temperatures, and secondarily upon other incidental characteristics which depend upon the service for which they are designed. A brief survey of the many methods proposed and in use by various operators for performing the various tests demonstrates the great need of a standard method of procedure for the testing of glues and gelatins and a scientific basis for their evaluation. Recent researches have brought to light many relationships that should be incorporated into a scheme of primary evaluation. From the chemists point of view gelatin is a pure protein and glue is a mixture of gelatin with the products of gelatin hydrolysis and other impurities in varying amounts. Commercial gelatin and glue should, therefore, from the standpoint of chemical constitution be primarily evaluated in terms of the proportion of pure and unhydrolysed gelatin which is contained in the material. From the point of view of the use of glue as an adhesive, glue should be evaluated in terms of the strength of the joint, produced under the most favorable conditions, which may be made with the material. The first point of view coincides with the latter in that the glue with the largest amount of unhydrolysed gelatin produces the strongest joint. The direct determination of either the gelatin content or joint strength is difficult and impractical for routine control and hence the control should be made by measuring some variable which has been found to be directly dependent upon these properties and which would express them properly. The author's work has shown that if the viscosity be held constant the jelly content and joint strength will vary as the jelly consistency while if the latter be held constant these properties will vary as the viscosity. The jelly consistency and the viscosity are also shown to bear the same relation to the melting point while the latter appears to define with precision the gelatin content and the joint strength. There are many methods by which the melting point may be determined, but most of these are inexact. The author found that by plotting the curve of viscosity at regularly decreasing temperatures and extrapolating to the temperature where the viscous flow would be *nil* the figures obtained corresponded well with those obtained by several methods of melting point determination. But it was observed that the same order of differentiation could be obtained by merely taking the viscosity measurements at 32° to 35° C. and that such results were precisely indicative of the gelatin content and joint strength of the product. As a rational system of evaluating glues and gelatins the author suggests that (1) the viscosity determination be made by means of the MacMichael viscosimeter at 35° C. using the equivalent of 18 grams of dry glue made up to 100 grams with water. The result should be expressed in centipoises. (2) The H-ion concentration be determined on a 1 per cent solution. For the purpose of secondary evaluation it is suggested (1) that the viscosity of 60° C. may be of use in some cases, to determine the viscosity at working temperature. (2)

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The jelly consistency may be determined by use of the instrument described by the Forest Products Laboratory [*Tech. Notes,* **F32** (1919)] and expressed in millimeters of depression; or for more exacting requirements, the more elaborate and scientific method of Sheppard [*J. Ind. Eng. Chem.,* **9**, 523 (1917)] may be used to advantage. (3) The foam test may be made in a standard glass, by means of an egg beater turned at about 4 revolutions per second for 30 seconds and measured after 10 seconds as millimeters of foam. (4) The grease test may be made by making a streak of the glue, to which a dye such as turkey red has been added, on a sheet of paper. (5) The appearance may be specified according to the information desired. (6) The odor should be noted in a warm solution and a strong or sour odor should not develop within 48 hours at 30° to 40° C. In some cases special tests will be required, as for ash, precipitation with aluminum salts, etc.; in the case of gelatin for edible purposes copper, zinc, arsenic, sulfur dioxide and qualitative tests for preservatives may be made. The author suggests that the grade designation of the product, as ascertained by the primary evaluation, may be conveniently expressed by consecutive numbers, 1 being the lowest, following the initial letter of the type of product. Thus hide glues may be designated as H_1, H_2 and so on up to perhaps H_{15} and bone glues as B_1, B_2, etc. If the primary evaluation is measured as suggested, by a determination of the viscosity of an 18 per cent solution (dry basis) at 35° C. and expressed in centipoises, then H_1 or B_1 is to correspond to a viscosity of less than 20 centipoises and each succeeding numerical increase in the designation is to correspond to an increase of 10 centipoises. Thus H_2 or B_2 will equal 20-29 centipoises and H_{15} or B_{15} from 150 to 159 centipoises. A complete bibliography is appended. G. W. S.

Durability of Sole Leather Filled With Cellulose Sulphite Extract. By R. C. Bowker. *Hide and Lea.*, Apr. 22, 1922, p. 13. American tanners have not been successful in their attempt to tan hides with sulphite cellulose extract, and it is generally considered as having no place in the tan-yard. It has found, however, a wide application as a filling material in the manufacture of sole leather. After the hides have been thoroughly tanned in the yard they still lack the firmness and weight required. It is the general commercial practice to produce these qualities by filling the leather with tanning materials by drumming, tempering and dry dipping.

Since the opinion has often been expressed that sole leather filled with this extract is inferior and since no known data on the subject were in existence, this investigation was made to determine the comparative durability of sole leather filled with sulphite cellulose extract and sole leather filled with the ordinary vegetable tanning materials.

Four different leathers obtained from three different tanners were used in this investigation. Of each kind of leather there were two lots:— One filled with the ordinary tanning materials and the other with sulphite cellulose extract. In each case, in general, both lots received the same treatment in tanning.

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After the leather was received at the laboratory full soles were cut and matched for test in a manner similar to that described in Bureau of Standards Technoligic Paper No. 138. The soles of each pair were cut from similar locations on the same hide. One sole of each pair contained sulphite cellulose extract and one contained the ordinary vegetable tanning materials used in the tannery which furnished the leather.

The leather was subjected to actual wearing tests on laborers, laboratory workers and office workers. The conditions of service were not uniform for all the different pairs of soles, some of which were worn on concrete floors, in machine shops, in boiler rooms, or in outside weather conditions.

TABLE I.—RESULTS OF WEAR TESTS.

No. pairs of soles tested	Ave. iron per sole		Days wear per sole		Days wear per iron	
	O	S	O	S	O	S
Lot No. 1—73	9.21	9.66	118.7	115.7	11.97	11.98
Lot. No. 2—90	9.80	9.54	94.4	90.5	9.84	9.49
Lot No. 3—54	8.69	8.51	59.6	58.1	6.86	6.83
Lot No. 4—63	8.44	8.48	63.7	67.9	7.55	8.01
Averages	9.18	9.05	84.1	83.1	9.06	9.08

O—Soles filled with ordinary vegetable tanning materials.

S—Soles filled either entirely or partially with sulphite cellulose extract.

The results are summarized as follows:—

1. Leather filled either partially or entirely with sulphite cellulose extract is as durable as leather filled with the ordinary tanning materials such as chestnut and quebracho. 2. As reflected by the chemical analyses this extract is as firmly fixed in the leather as these vegetable tanning materials. 3. The use of such a material instead of chestnut and quebracho would conserve these materials for use in the actual tanning process for which they are suitable and for which sulphite cellulose extract has not been successfully used. 4. It is probable that this material could be used as a filler in place of the more soluble glucose thereby producing a more waterproof leather. 5. Leather filled with this material can be made of as light and uniform a color as leather filled with the ordinary materials. This was the case for Lots No. 1 and 2. There was a slight difference in the color in Lots No. 3 and 4, the leather filled with sulphite cellulose extract was a little darker. 6. Using this material as a filler has no more effect on the aging of the leather than the ordinary materials since samples of these leathers, which have been in the laboratory for over two years, are still in a satisfactory and pliable condition. G. W. S.

Contribution to the Biological and Chemical Previous History of Hide and Pelt. III. The Mineral Constituents of Hide and Pelt. BY W. MOELLER. *Zeitschr. für Led. und Gerb. Chem.*, 1, 115 (1922). Many investigators have concerned themselves with the question of the technical and physiological importance of the mineral constituents of hide and leather. It has been proposed that the mineral constituents of hide determine, to a large extent, the characteristics of some leathers. In the older tanning literature the importance of silicic acid in the leather or tanning materials for the

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quality of leather is mentioned as is also calcium phosphate and alkalies The original ash content and the constituents of the ash are altered by salting, soaking, liming and bating. The impurities in the salt, and in the water such as hardness, and changes brought about by liming and bating may all influence the quality of the finished product. This investigation is confined to the change in ash content of hide on washing with distilled water and on liming and bating. The experiments were conducted by adding a definite amount of water to a definite amount of hide and after a definite time the water was replaced until 6 washings were made. The hide was analyzed for mineral constituents and the organic and mineral constituents were determined in each washing. From these experiments it is concluded that the mineral constituents removed from hide in the soaking process are very considerable and that the amounts of each are different. After a definite amount of soaking the relative ash content of the hide and the percentage composition of the ash remains fairly constant. The mineral constituents washed out on prolonged washing hold the same ratio to the hydrolysed hide substance as the ash constituents of the pelt. Silicic acid and lime salts predominate in the ash of pelt after washing. In the process of liming and bating the absolute amount of ash in the hide is not changed but the majority of the silicic acid is dissolved out and replaced by lime. It may be because of the latter that the sweating process is preferred to liming for unhairing for the production of good sole leather. G. W. S.

The Relation Between Hydrolysis and Adsorption III and IV. By W. MOELLER. *Zeitschr. für Led. und Gerb. Chem.*, 1, 125 (1922). The hide which is found in a weakly hydrolytic state is decomposed according to the kind of acid or alkali used into material which attains all degrees of dispersion, as molecular complexes, individual molecules and finally as cleavage products of these molecules of the original protein complexes. In this way is liberated principal and auxiliary valences parallel with the strength of the acids and the result is an apparent chemical reciprocal action between the hide as a whole and the acid The same holds true of gelatin. Because of numerous criticisms of the previous work on the relation between hydrolysis and adsorption this work was repeated and it was confirmed in principal. The existence of a maximum of hydrolysis after a determined time of action of the acid on hide powder was determined. The dependence of hydrolysis and adsorption of acid by the hide powder on the degree of dispersion of the hide powder was determined. By increasing the degree of dispersion of the hide, the hydrolysis was found to be independent of the concentration of the acid. By the use of a large volume of hydrochloric acid deviations occur in the hydrolysis and adsorption from results obtained when using a small volume which is attributed to the unhindered diffusion of the decomposition products from the hide and removal of the maximum of hydrolysis to a materially longer time period. G. W. S.

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Halogenolysis of Hide. A Contribution to Halogen Tannage. By W. MOELLER. *Zeitschr. für Led. und Gerb. Chem.*, 1, 146 (1922). As a resnlt of tanning experiments with halogens and gelatin, Meunier and Seyewitz concluded that it appeared that only chlorine and bromine had a tanning action while iodine was unable to render gelatin insoluble. The latter is contradictory to practical usage as iodine finds extensive application for the production of catgut. Experiments were conducted using 4.4 gram portions absolutely dry hide powder to varying amounts of the three halogens—chlorine, bromine and iodine—in aqueous solution. The time intervals for the experiments were 1, 8, 14 and 30 days using separate samples for each time period. The experiments with chlorine were conducted with 1,000 cc. of solution while 100 cc. were used for bromine and iodine. After the given time intervals the solutions were filtered through glass wool and nitrogen determined in an aliquot of the filtrate by the Kjeldahl method. In a second aliquot the halogen was determined titrimetrically. From the results it is concluded that the action of chlorine and bromine in aqueous solution on hide consists of a tanning action which is principally an oxidation process and besides this a considerable decomposition of the hide which leads to the formation of halogen acids. The action of iodine is exclusively a tanning action without decomposition of the hide The amount of halogen taken up by the hide within the various concentrations and time intervals of these experiments is approximately the same for all three. G. W. S.

The Action of Lactic and Butyric Acids on Hide Substance. By W. MOELLER. *Zeitschr. für Led. und Gerb. Chem.*, 1, 153 (1922). Lactic and butyric acids assume an important role in the swelling of pelt. Although mineral acids are used it is simply because of the materially lower price and not because their use are an advantage in respect to enhancing the quality of pelt or the finished leather. There is a difference of opinion between the practical and the theoretical man as to their action and use. In the literature we find some advocates of the opinion that these organic acids should not be used especially for deliming as they attack the hide and cause a great loss of hide substance. Others advocate their use as excellent deliming agents that do not attack hide substance at all. The experimental work of this paper is confined to the determination of the extent to which hide powder is hydrolysed by these two organic acids and, to some extent, the amount of acid adsorbed by the hide. The experiments were carried out, using 1,000 cc. of solutions of lactic and butyric acids in concentrations of 1/100, 1/20, 1/10 and 1/2 normal. Four and four-tenth grams was placed in each solution and after thoroughly mixing they were allowed to stand for time intervals of 1, 8 and 14 days and 3 and 4 weeks. The hide substance hydrolysed was determined by nitrogen determination on the filtrate. In some cases the hide substance was determined on the filtrate after filtering with the use of kaolin too. The latter would give only the hide substance which was molecularly dispersed while the ordinary filtration also included hide substance which

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was present in the colloid state, the hydrolysis not having proceded far enough to have split the hide substance into protein molecules or decomposition products of the protein molecule.

The results with lactic acid show that, without the kaolin filtration, the amount of hide substance in solution is from two to three times as much as is given by pure water. With the kaolin filtration there is hardly a material difference. There is a slight tendency to an increase in hydrolysis with increasing concentration of acid. The results with butyric acid are slightly lower than those with lactic. There is practically no increase in hydrolysis with either increasing concentration or increased time of contact. It is found that in the 1 day period lactic acid is increasingly adsorbed with increase in concentration of acid. After 8 days there is an increase in the amount adsorbed from the weaker solution but a decrease in the stronger ones until a negative result is obtained with the strongest. Butyric acid exhibits a regular increase in the amount adsorbed by the hide with increase in concentration of acid and increased time of contact. The value of these acids is in giving the greatest possible swelling with the least possible hydrolytic decomposition of the hide. G. W. S.

Belt Grease. Anon., *Ledertech. Rund.*, 14, 28 (1922). Only good, materials and pure fats should be considered for use on belts. Substances like resins and weighting materials like lime, chalk barytes, etc., should be avoided as all such damage the belt. Any oil or fat cannot be used satisfactorily for belt. The purer and better the materials the greater will be the elasticity and servicability of the belt. A mixture of bees wax and neatsfoot oil (1:10) gives an excellent preserving and adhesive belting grease. From 1 to 2 parts tallow and 3 parts train oil is a good grease to which sometimes is added about a tenth of its weight of powdered graphite. Other formulae given are as follows:—(1) 4 kgs. of castor oil, 800 grams tallow, 16 grams powdered gum and 18 grams finely powdered borax. (2) 2 parts tallow, 1 part castor and 1 part train oil. (3) 9 parts linseed oil and 4 parts litharge are boiled with some water until the mixture begins to form a tough mass, after allowing to cool somewhat, turpentine and rapeseed oil are added until the mass assumes a cream like character. (4) 1 part tallow, 4 parts fish oil, 1 part rosin and 1 part pure wood tar.

Belts should be well greased but not excessively so. They should be well cleaned and then greased every quarter year. G. W. S.

PATENTS

Leather Substitute. U. S. Patent 1,409,301. W. KING AND W. L. KING, Victoria, British Columbia, Canada. Filed October 28, 1919. Serial No. 334,091. The herein described means for producing a waterproof sole for shoes consisting of mixing and boiling together, asphalt, leather dust, cotton fiber and linseed oil, and thereafter subjecting the mass to a hydraulic pressure to form the same in a sheet.

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Leather Splitting Machine. U. S. Patent 1,410,703. J. A. MEYER, Newark, N. J. Filed Oct. 9, 1919. Serial No. 329,420.

Process of Making a Leather Substitute. U. S. Patent 1,411,376. R. B. RESPESS, New York, N. Y., assignor, by mesne assignments, to Respro, Inc., Cranston, R. I., a Corporation of Rhode Island. Filed March 31, 1920. Serial No. 370,139. The herein described process of making a leather substitute consisting in treating a woven fabric in a napping machine to produce a loose fiber surface on the fabric, saturating the fabric with a binding agent, subjecting to pressure, drying the sheet and pressing under tension.

Tanning. U. S. Patent 1,413,488. W. H. OCKLESTON, Bourn, and T. B. CARMICHAEL, Waterloo, near Liverpool, England. Filed Jan. 21, 1922. Serial No. 530,955. A method of tanning which includes the step of subjecting the material being tanned to the action of pyridine.

Means for Greasing Leather of all Kinds and for Oil Tanning. U. S. Patent 1,414,044. O. RÖHM, Darmstadt, Germany, assignor, by mesne assignments, to The Chemical Foundation, Inc., a Corporation of Delaware. Filed June 13, 1917. Serial No. 174,642. The process for preparing a tanning material which comprises mixing with an oil moderately heated, from one-half to one per cent sulphuric acid, and neutralizing the mixture with a caustic alkali. An agent for greasing leather and for oil tanning, consisting of a vegetable oil embodying from about one-half to one per cent of sulphuric acid.

Tanning. U. S. Patent 1,414,045. A. RÖMER Stuttgart, and L. BLANGEY. Mannheim, Germany, assignors, by mesne assignments, to The Chemical Foundation, Inc., a Corporation of Delaware. Filed Sept. 2, 1916. Serial No. 118,286. The process of tanning which comprises treating hide in a bath containing an aromatic sulfonic acid derived from an aromatic hydrocarbon containing within its molecule at least two aromatic nuclei, said nuclei being united by at least one polyvalent atom.

Process for the Manufacture of a Tanning Material. U. S. Patent 1,414,312. C. SORGER, Wilmington, Del. Filed June 25, 1921. Serial No. 480,471. Process for the manufacture of a tanning material from sulphite liquor which consists in treating the thickened liquor with so much acid sulfate of alkali salt that the whole lingo-sulfonic acid is precipitated as alkali salt.

Process of Treating Hides and Hide Treating Apparatus. U. S. Patent 1,414,404. C. J. GLASEL. New York, N. Y. assignor by mense assignments, to L. H. GLASEL, New York, N. Y. Filed April 12, 1917. Serial No. 161,449. The process of treating hides and skins secured within a receptacle, comprising moving the hides and skins therein working them from points other than their suspension and circulating a tanning medium within the container without stopping the motion of the containers.

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Tanning. British Patent 173,508. J. BYSTON, Holstein, Germany, and BARON VON KARL VIETINGHOFF, Berlin. Dec. 22, 1921, No. 34,549. Mineral tanned leather is retanned with organic tanning-agents in three stages. After rinsing to remove any uncombined mineral salts, the leather is placed in an organic tanning solution of about 50° Bé., the acid formed in the reaction being continually neutralized with alkali until permanent neutralization is obtained. The second stage consists in treating the product with a solution of an alkali salt of an organic tanning matter until it is thoroughly saturated. The substances incorporated in the leather are finally precipitated by reaction with a corresponding quantity, ascertained by analysis or otherwise, of a solution of neutral or alkaline chromium, iron, or aluminium salts, so that the final product does not contain any uncombined metal salts. The leather thus obtained is allowed to rest for a few days, is then rinsed ,and treated in the usual manner.

Tanning-Agents. Mordants. British Patent 173,757. GERB-UND FARBSTOFFWERKE H. RENNER & Co., AKT.-GES., Hamburg, Germany. Dec. 30, 1921, No. 35,064. Coumarone resins are sulphonated with concentrated or fuming sulphuric acid and the product then treated with salts, particularly oxides, hydroxides, and carbonates, of iron chromium, or aluminium. The resulting metal sulphonates are soluble in water and can be used for tanning and mordanting purposes by reason of their precipitating effect.

Tanning. British Patent 173,853. W. T. CLARK, London.—(*Chemische Fabriken Worms Akt.-Ges.; Frankfort-on-Main, Germany.* Oct. 5, 1920, No. 28,247. Instead of using iron formate for tanning hides, as described in the parent Specification, a tanning-material made by partial double decomposition between an iron salt and a formate is used.

Synthetic Tanning-Agents. British Patent 173,881. J. Y. JOHNSON, London.—(*Badische Anilin and Soda Fabrik; Ludwigshafen-on-Rhine, Germany*). Oct. 11, 1920, No. 28,749. Naphthalene, anthracene, phenanthrene, or other hydrocarbon at least bicyclic, or carbazole, or a halogen or sulphonic acid substitution product, is condensed with a carbohydrate, such as cellulose, starch, or their conversion products down to glucose, or with other sugars, in such a way that sulphonic acid groups are contained in the final product; that is to say, sulphuric acid is used as a condensing agent when a sulphonic acid is not employed as a reaction material.

Treating Hides etc., British Patent 174,383. H. C. MARRIS AND W. WALKER & SONS, LTD., Bolton. Dec. 29, 1920, No. 8,861. Tanning-pits are supplied with liquor through distributing-pipes provided at intervals with flexible delivery pipes serving a number of adjacent pits. The liquor is circulated by a pump arranged in or in connection with a supply tank, which is replenished from a storage tank either by means of a traveling tank or vat or by piping, the levels being so arranged that the transfer or liquor is effected by gravity.

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BUREAU OF EMPLOYMENT

THE AMERICAN LEATHER CHEMISTS ASSOCIATION

Notice of positions vacant and situations wanted will be kept on file at the Secretary's office.

Prompt co-operation of the chemists in the trade will result in a mutual benefit to those seeking employment and those desiring chemists.

POSITION VACANT

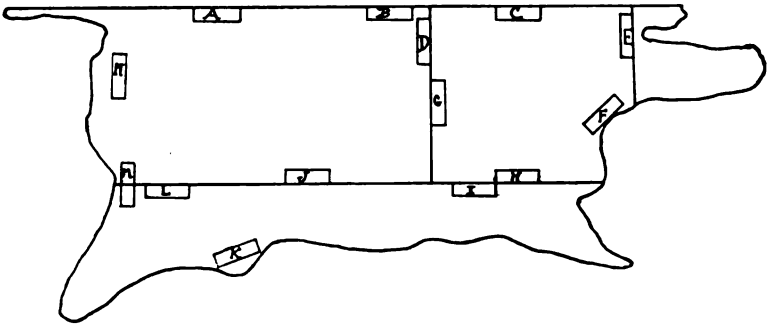
ASSISTANT CHEMIST—Position vacant in tannery laboratory. Person with experience desired. For information communicate with the Secretary.

ADOPTION OF PROVISIONAL METHOD

The following method for Sampling Leather has been voted by the Association as a provisional method:

SAMPLING LEATHER

To sample any one of the ordinary commercial cuttings of leather, samples must be cut from each piece sampled of the size and in the locations designated below.



	Single	Double
Belly	I-L-K	——
Shoulder	C-H	G-H
Bend	A-B-J	N-D-J
Butt	A-C-J	N-E-J
Side	A-C-K	N-F-M

It is much more difficult to sample satisfactorily double than single bends, butts and hides and wherever possible, the sampling prescribed for single bends, butts and hides should be followed.

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The location of the samples is shown only relatively, because of the wide variation in the size of hides, skins, etc., but the relative location shown in the diagram must be adhered to strictly.

Each sample is to be cut of rectangular shape, approximately 2½ inches x 8 inches, ½ inch then being removed from the uncut edge so as to leave the final sample for analysis exactly 2 inches x 8 inches. The whole of each sample is to be prepared for analysis by sawing, planing or other approved method and the leather so prepared from each sample must then be mixed with most scrupulous care to insure a uniform mixture. Equal weights are now taken from each of the prepared samples obtained from the piece sampled, and these, when thoroughly mixed together, constitute the sample for analysis.

When samples are taken from more than one piece in any one lot, all samples from the location are to be prepared as above—thoroughly mixed and then equal weights taken from each of the mixtures so obtained to constitute the sample for analysis.

Sawed leather is exceedingly difficult to mix and unless exceptional pains are taken with the mixing to insure a uniform mixture, a representative sample will not result.

AMERICAN OIL CHEMISTS SOCIETY
13th ANNUAL CONVENTION

The Annual Convention of the American Oil Chemists' Society was held this year in New Orleans on June 7th and 8th. This Society has adopted the plan of the A. S. T. M. and other scientific organizations of having its committee reports printed and distributed at the meetings. These reports were discussed and expeditiously disposed of leaving plenty of time for the consideration of a number of important papers.

Dr. Geo. S. Jamieson, Chemist in Charge of the Oil, Fat and Wax Laboratory of the U. S. Bureau of Chemistry, presented some of the results of his laboratory's investigations of the composition of cotton-seed oil in a paper on "The Analysis of Crude Vegetable Oils." He outlined a method for the determination of the actual quantity of pure glycerides present and said

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that there were other substances in cotton-seed oils beside free fatty acids which combined with caustic soda in the usual refining processes. A small quantity of these had been isolated and it was proven they contained phosphorous and other inorganic radicles. When the chemical identity of the non-fat bodies in oils has been determined and their effect upon commercial refining operation is known, it will be much easier than at present to judge of the efficiency of factory refinings.

Dr. David Wesson, Technical Director of the Southern Cotton Oil Co., exhibited the new E. K. Colorimeter, which he has been studying as a possible solution of the present difficulties in satisfactorily grading oils for color. He also showed lantern slides of another instrument which is being perfected by the Kueffle & Esser Co. and a number of color absorption curves of oils and Lovibond glasses. These curves for refined cotton-seed oils show a striking depression at one point which is nearly eliminated by bleaching with fuller's earth. Dr. Wesson said that with the K. & E. instrument it would be possible to tell when an oil had been partly bleached and also whether or not any given refined oils were bleachable.

The silver loving cup for most accurate work in the determination of both oil and ammonia in thirty-eight samples of oils used in meals, which is given annually by the Society, was awarded at the banquet, to Mr. H. B. Battle. A number of certificates for proficiency in the analysis of oils, fertilizers, soap stock and fats were distributed by Mr. Herbert Bailey, Chief Chemist of the Southern Cotton Oil Co., as a part of his report on the work of the Co-operative Analytical Program.

The Society voted to incorporate under the laws of the State of Louisiana and after the final session the officers for the coming year went to their attorney and signed the incorporate papers.

For the ensuing year the following officers were elected: President, L. M. Tolman; Chief Chemist, Wilson & Co., Chicago; Vice-President, H. B. Battle, of Montgomery, Ala.; Secretary-Treasurer, Thos. B. Caldwell, Wilmington, N. C.; Editor, Chemists Section, Cotton Oil Presses, Herbert Bailey, Savannah, Ga.

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THE BACTERIOLOGY OF FRESH STEER HIDE*

By George D. McLaughlin and George E. Rockwell

FROM THE DEPARTMENT OF LEATHER RESEARCH OF THE TANNERS' COUNCIL IN THE UNIVERSITY OF CINCINNATI, WITH THE COLLABORATION OF THE DEPARTMENT OF BACTERIOLOGY AND HYGIENE

Received June 9, 1922

Any contention that bacteria or their enzymes play an important role in the curing and tanning of hides is almost superfluous. Their presence and activities have received much attention in the past.[1] Valuable as these contributions have been, especially the revolutionizing work of Wood, there has been no systematic study of bacteriology of tanning as a whole; and the subject will not become clear to us until we understand the action of bacteria in each successive step of the process. We have, therefore, begun our work by studying the bacteria of the fresh hide.

To isolate and catalog all of the bacteria derivable from a fresh hide, soak, lime, or tan-vat would be an endless and probably useless task, since the next hide or vat may show a different flora. To divide bacteria, however, into groups, characterized by general characteristics and amenable to group control is practical. For the present, we will divide them into proteolytic (those which liquefy solid protein), and non-proteolytic (those which do not liquefy solid protein, or to a very slight extent only).

In the first part of this communication, we will show that hide contains many kinds of bacteria, which will exert varying effects upon it. In the second part we will show the effects of the proteolytic and non-proteolytic groups of bacteria upon hide, and how their activity may be stimulated, controlled or prevented.

* Read at the 19th Annual Meeting of the A. L. C A. at Bigwin Inn, Canada, June 21, 1922.

[1] The more important studies are as follows: The Origin of Salt and Iron Stains by: Abt.—*LaHalle aux Cuirs*, July 28, 1912 (reprinted This JOURNAL, 7, 492 (1912); *Collegium*, 1912, p. 388-408; *Ibid*, 1913, p. 204-206, 439. Becker—*Collegium*, 1912, p 408. Paessler—*Lederlechn. Rundschau*, 1912, p. 137; *Ibid*, 1921, p. 169. The Bacteriology of Soaks and Vegetable Tan-liquors by Andreasch, *Der Gerber*, 1896, p. 911. *Ibid*, 1897, p. 52, 248, 341, 620, 747, 925 and 1025. The Bacteriology of Liming by Schlichte. *J. A. L. C. A.*, 10, 585 (1915). The Bacteriology of Bating—Wood, Becker and Popp and the Bacteriology of Drenching, Wood and Wilcox; see "The Puering, Bating and Drenching of Skins," J. T. Wood, London, 1912. The Enzymatic Conversion of Tannin into Gallic Acid—Fernbach, *Comptes Rend.*, 26, 1214 and *J. S. C. I.*, 20, p. 137 (1901).

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PART I

Thirty short-hair steer hides, free from manure, were sampled separately, as they dropped from the carcass. Part of each sample was soaked in sterile water, another part in sterile nutrient broth media. This procedure was extended to cover an incubation temperature range of 12° to 56° C. In each case, the hide was allowed to remain in the media until marked putrefaction occurred. The resulting growths of micro-organisms in the media were then examined, both microscopically and culturally, and their morphological and biological characteristics determined.

It is most important to remember that we are dealing with *hide*. To show that bacteria have a certain effect on gelatine, blood serum, or other protein, does not necessarily mean that their effect will be the same on hide.

We studied the bacterial action on fresh hide in several ways; through the appearance of the treated hide; by whether the hide's capacity for swelling is changed; and by the extent to which the hide has been dissolved or decomposed.

Having established that bacteria act on hide, it is essential to know what part of the hide has been affected, since hide is composed of not one component, but of a number. In order to accomplish this, one must isolate the several hide protein fractions with care, as we have found the ordinary methods of preparation yield fractions which bacteria cannot utilize. The albumin and globulin as well as the mucoid fractions must be extracted and dialyzed in the ice box; toluene is the proper antiseptic to use in the enzymatic digestion of elastin in preparing collagen; and the drying of all fractions must be performed in a rapid current of air, and at a temperature not exceeding 35° C.[2]

It will be noted from Table I that in addition to determining the action of bacteria on various hide proteins (from which keratin is for the present omitted), we have recorded their action on the following culture media; seventeen carbohydrates, gelatine, coagulated blood serum, potato, coagulated egg and milk. Indol production and nitrate reduction are also given. The aerobic and anaerobic nature, the growth in lime solutions of various

[2] The detailed description of the protein components of hide and their isolation will be dealt with in another publication.

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TABLE I.

Strain number	Size and shape	Gram stain	Spore	Motility	Colony on agar	Growth in Media Containing Lime				Remarks	Source
						¼ Sat.	½ Sat.	Sat.	Excess		
I	Small bacillus	—	—	+	Amoeboid, convex, opaque center	++	++	—	—		Hide No. 11
II	Large bacillus	+	+	+	Flat granular lobate edge, dark center	—	—	—	—		Hide No. 12
III	Staphyloccus	+	—	—	Capitate, even edge, light periphery opaque center	+	+	—	—		Hide No. 14
IV	Medium size bacillus	+	+	+	Amoeboid, grumose bluish translucent	±	±	—	—		Hide No. 15
V	Small bacillus	—	—	+	Raised opaque center, light periphery, erose edge	—	—	—	—	Produces NH_3	Hide No. 5
VI	Small bacillus	—	—	+	A spreading translucent growth	+	++	—	—		Hide No. 16
VII	Small bacillus	—	—	—	Convex, brownish opaque center, light periphery even edge	+	—	—	—	Produces NH_3	Hide No. 22
VIII	Large bacillus	+	+	+	Convex, opaque center fimbricated, translucent periphery	±	±	—	—		Hide No. 17
IX	Large bacillus	+	+	+	Raised, erose with a dark circular veinlike						

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concentrations and the optimum temperature of growth is shown. This elaborate identification system is necessary, otherwise, with less data, such as the usual number of proteins and carbohydrates, separate and distinct bacteria may not always be differentiated.

The microscopical study of both hanging drop preparation and stained smears from the mixture of micro-organisms that grew upon placing the fresh hide in sterile water and sterile nutrient broth media, revealed a widely diversified flora, including: cocci, staphylococci, streptococci, both gram positive and gram negative; bacilli, large and small, motile and non-motile, both gram positive and gram negative; spirilla, spirochaeta, also yeasts, oidia, molds, and protozoa.

From the entire group we selected twenty-four strains which predominated. Their characteristic action on the various media appear in Table I. The forms of ten strains are shown, both as to colony formation on agar and their individual morphology by the micro-photographs which follow.

Part II

Having established that the decomposition of fresh hide results in the presence of micro-organisms of both proteolytic and non-proteolytic type, we will show what actual effect each group has on fresh hide.[3]

Since corium constitutes the bulk of the hide, we have used it for these experiments, thus eliminating any possible variables arising from the presence of blood, fat or extraneous matter, present on the whole fresh hide.

The bacteria with which we inoculated the corium consisted of two mixtures, 1, of proteolytic bacteria, and 2, of non-proteolytic bacteria, isolated from a broth solution in which a piece of fresh hide had decomposed.

The experimental corium was placed in sterile water within thirty minutes from the time it left the carcass of the animal, which prevented any drying out of its surfaces. After standing in the water for a definite period of time, it was removed and placed in saturated lime solution, containing excess lime, for twenty-four hours. One piece was used as a control, another

[3] In another place, we will show that the presence of blood and extraneous matter, which is present under operating conditions, enormously increases the action of the proteolytic bacteria.

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piece had a mixture of the proteolytic bacteria smeared on its surfaces before placing in the water soak, while the third piece had a mixture of non-proteolytic bacteria smeared on its surfaces. The results are shown in Tables II and III. In the experiments summarized in Table II, the corium was merely cleaned, while in those in Table III it was cleaned and then sterilized by being placed in hydrogen peroxide for one and one-half hours at 51° C. before inoculation. Part of this series of experiments is shown in Figure 1.

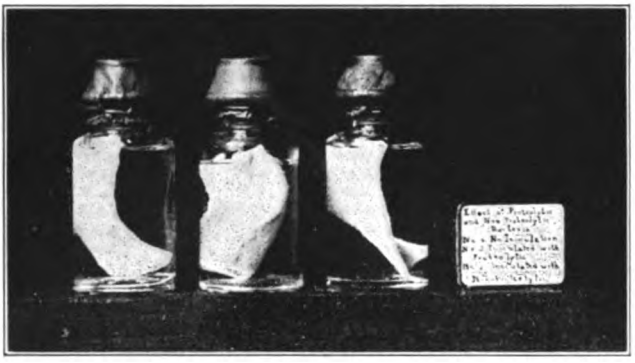

Fig. 1.—Corium at left uninoculated.
Corium in middle inoculated with proteolytic bacteria.
Corium at right inoculated with non-proteolytic bacteria.

From Tables II and III we note that corium inoculated with proteolytic bacteria shows loss in swelling ability, is depleted and is decomposed as compared with the uninoculated control; whereas inoculating corium with non-proteolytic bacteria results in a plump and healthy condition and produces no decomposition.

Bacterial growth and activity depend upon nutritive conditions, physical condition (temperature), acid or alkaline reaction of the environment, and respiratory conditions. Of these factors, which are the most favorable for the growth and activity of the proteolytic and non-proteolytic groups respectively? Let us consider each of these conditions separately.

1. *Nutritive Conditions.*—How do variations in food supply affect bacterial life on a hide?

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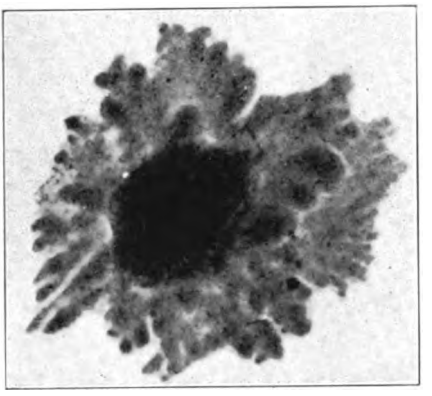
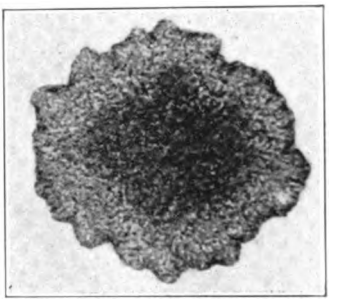


Colony of Strain No. 1.



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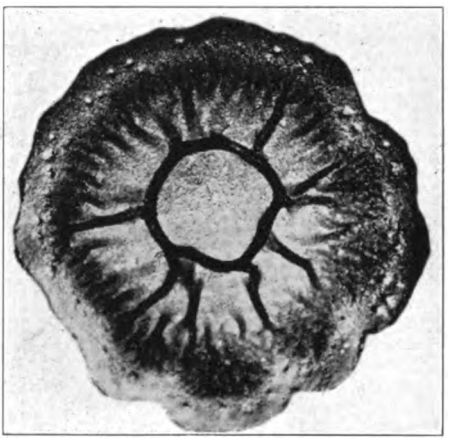

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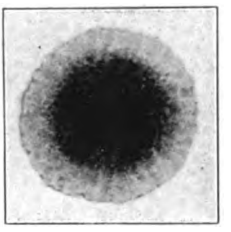

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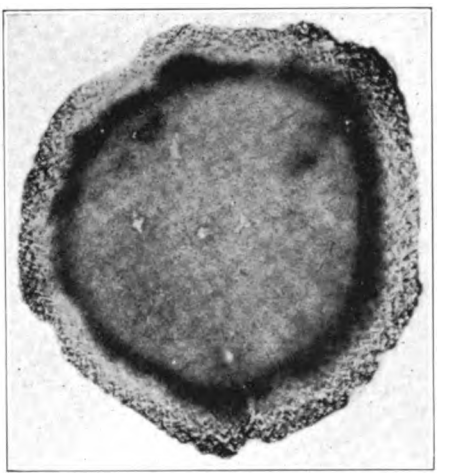

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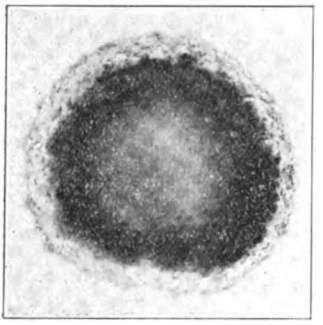

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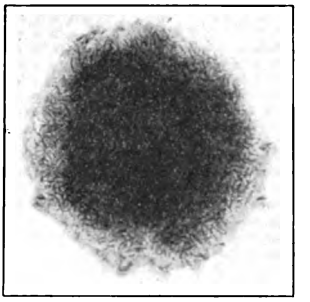

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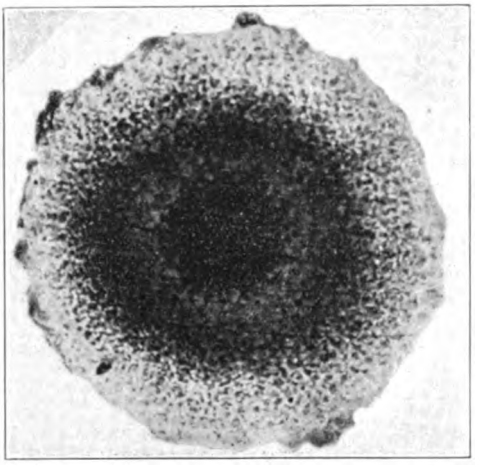

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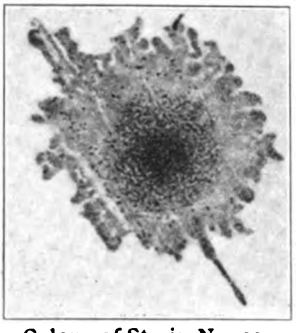

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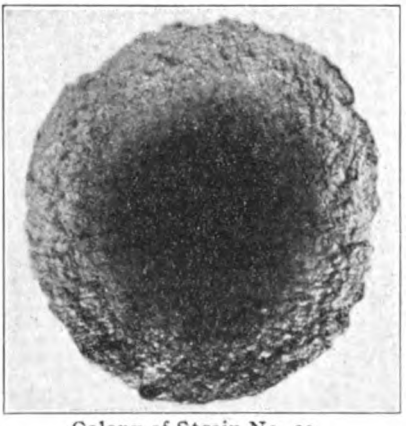

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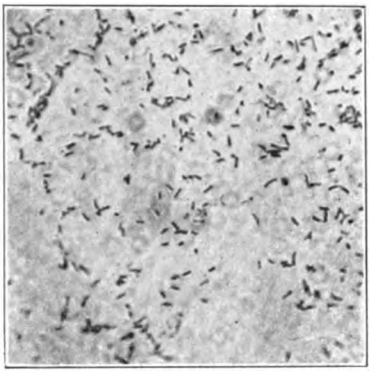

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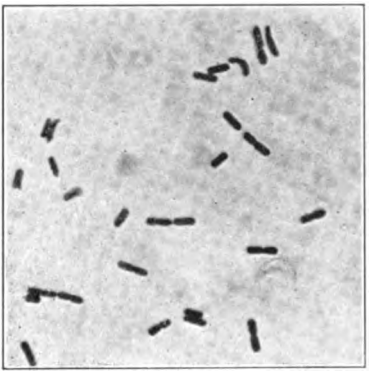

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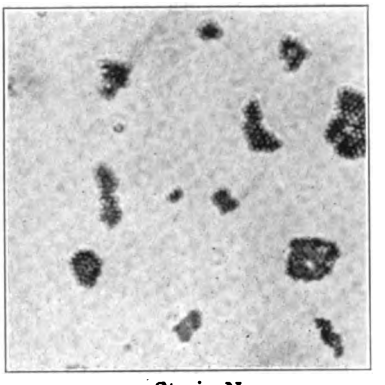

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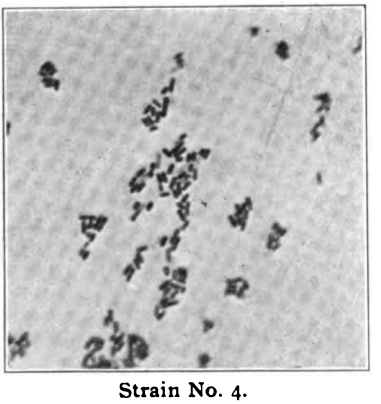

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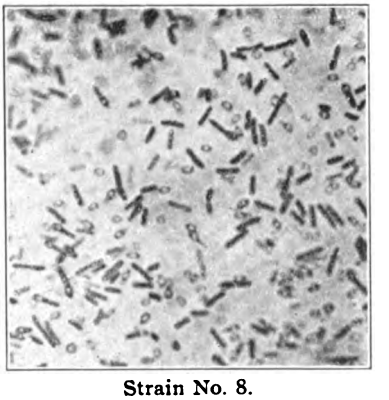

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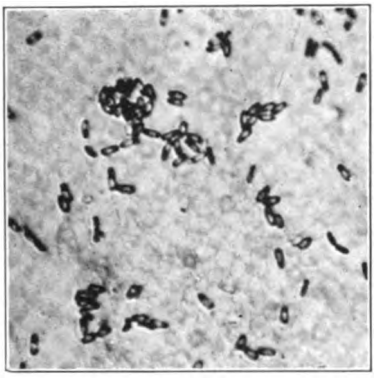
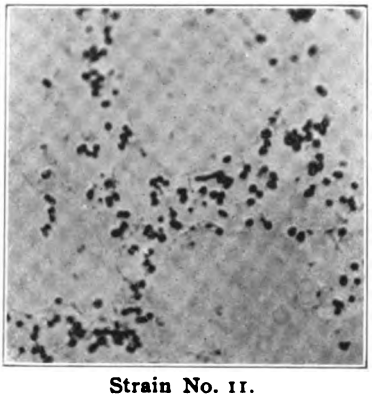


Strain No. 9.

Strain No. 10.



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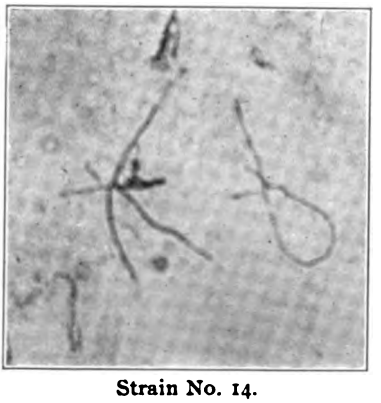

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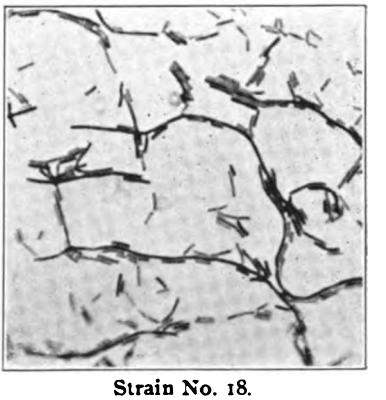

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TABLE II.—25 GRAMS OF CORIUM, 250 CC. OF WATER, AND 250 CC. OF LIME SOLUTION WERE USED IN EACH INSTANCE

Hours in water at 20° C.	Bacterial inoculation	Per cent weight gain in water	Per cent loss in water	Per cent white weight gain after 24 hrs. in lime solution at 20° C.	Per cent loss after treatment with lime solution	Per cent total white weight gain	Per cent total loss	Appearance and decomposition of hide
48	None	2.48	-	4.39	-	6.87	-	Fair, slight decomposition
48	Proteolytic	1.91	-	3.42	-	5.33	-	Poor, definite decomposition
48	Non-proteolytic	3.07	-	6.63	-	9.70	-	Very good, no decomposition
72	None	1.44	-	3.65	-	5.90	-	Fair, slight decomposition
72	Proteolytic	-	0.36	-	2.94	-	3.30	Depleted, much decomposition
72	Non-proteolytic	4.41	-	6.50	-	10.91	-	Very good, no decomposition

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TABLE III.—20 GRAMS CORIUM, 200 CC. WATER, AND 200 CC. LIME SOLUTION USED IN EACH INSTANCE

Hours in water at 20° C.	Bacterial inoculation	Hours in lime solution at 20° C.	Per cent white weight gain	Per cent loss	Appearance and decomposition
48	Sterile	24	3.76	–	Good, no decomposition
48	Mixed proteolytic	24	–	12.36	Depleted, decomposition
48	Mixed non-proteolytic	24	12.53	–	Excellent, no decomposition

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A piece of clean corium was divided into three pieces. These pieces were weighed, one was placed in sterile distilled water, another in a 3 per cent dextrose solution, while the third piece had a few drops of blood smeared on it and was then placed in sterile water. After soaking 48 or 72 hours the three pieces of corium were transferred to a saturated lime solution (containing excess lime) and at the end of 24 hours were weighed. The results were striking, as shown in Tables IV and V, and Figs. 2A, 2B and 3.

Fig. 2A.—Left-hand bottle Control
Middle bottle Blood
Right-hand bottle Dextrose

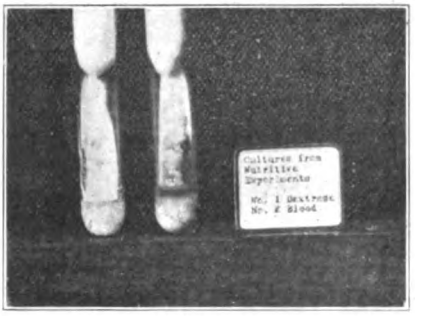

Fig. 2B.—Left-hand tube—Culture from dextrose solution shown in Fig. 2A.
Right-hand tube—Culture from blood solution shown in Fig. 2A.

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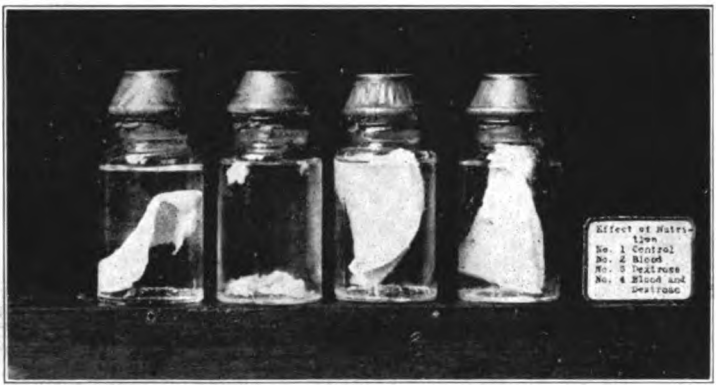

Fig. 3.—Same as Fig. 2A, except the fourth bottle, at right, has been added it contains both blcod and dextrose.

On studying Tables IV and V we observe that:

A. The addition of a few drops of blood to the corium produces a large flora of proteolytic bacteria on it, causing it to become depleted and decomposed and produces a loss of its ability to swell in a lime solution.

B. The addition of dextrose to the solution in which the corium stands, causes the growth of non-proteolytic bacteria, and results in a much swollen corium, a large white weight gain, and no decomposition.

Fig 4.—Left-hand bottle stood 24 hrs at 24° C. in H_2O and 24 hrs. in lime.
Next bottle stood 24 hrs. at 37° C. in H_2O and 24 hrs. in lime.
Next bottle stood 48 hrs. at 24° C. in H_2O and 24 hrs. in lime.
Right-hand bottle stood 48 hrs. at 37° C. in H_2O and 24 hrs. in lime.

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TABLE IV.—About 20 Grams of Corium. 250 Cc. of Water and 250 Cc. of Lime Solution Used in Each Instance

Hours in water at 20° C.	Food added to water or hide	Hours in lime solution at 20° C.	Per cent white weight gain	Per cent loss	Appearance of hide	Kinds of bacteria present in water surrounding hide
72	None	24	2.72	-	Fair	Few proteolytic and non-proteolytic
72	3 Per cent dextrose	24	20.55	-	Excellent, plump and healthy	No proteolytic, many non-proteolytic
72	Blood	24	-	71.59	Extreme decomposition	Large number of proteolytic

NOTE:—Part of the swelling noted with dextrose solution is doubtless due to fermentation products, directly or indirectly.

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TABLE V.—20 GRAMS OF CORIUM, 250 CC. OF WATER AND 250 CC. OF LIME SOLUTION USED IN EACH INSTANCE

Hours in water at 20° C.	Food added to water	Hours in lime solution at 20° C.	Per cent white weight gain	Per cent loss	Appearance of hide	Kinds of bacteria present in water surrounding hide
48	None	24	12.23	–	Fair	Few proteolytic and non-proteolytic
48	Blood	24	–	1.74	Poor	Many proteolytic
48	Blood + 3 per cent dextrose	24	19.06	–	Good	Few proteolytic and very many non-proteolytic
48	3 Per cent dextrose	24	13.39	–	Very good	Many non-proteolytic
72	None	24	0.59	–	Depleted	Quite a number of proteolytic
72	Blood	24	–	0.90	Decomposed	Many proteolytic
72	Blood + 3 per cent dextrose	24	14.86	–	Good	Many non-proteolytic, few proteolytic
72	3 Per cent dextrose	24	8.90	–	Excellent	Many non-proteolytic

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TABLE VI.

Corium soaked in sterile H_2O at	Time in water	Then in sterile $Ca(OH)_2$ at	Time in lime	Per cent weight gain	Per cent weight loss	Number of bacteria
24° C.	24 Hrs.	24° C.	24 Hrs.	5.97	–	Few
37° C.	24 Hrs.	24° C.	24 Hrs.	–	9.35	Many
24° C.	48 Hrs.	24° C.	24 Hrs.	1.68	–	Fair amount
37° C.	48 Hrs.	24° C.	24 Hrs.	Too decomposed to weigh		Very many

Cultures from each water solution show many bacteria, the number of which is increased tremendously by the higher temperature.

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TABLE VII. EFFECT OF SOAKING CORIUM IN STERILE H_2O AT DIFFERENT TEMPERATURES

Corium soaked in sterile H_2O at 8° C. for 24 hrs.	No decomposition	No bacteria
Corium soaked in sterile H_2O at 8° C. for 72 hrs.	No decomposition	No bacteria
Corium soaked in sterile H_2O at 8° C. for 268 hrs.	Slight decomposition	Few bacteria
Corium soaked in sterile H_2O at 20° C. for 24 hrs.	Slight decomposition	Few bacteria
Corium soaked in sterile H_2O at 20° C. for 48 hrs.	More decomposition	Many bacteria
Corium soaked in sterile H_2O at 20° C. for 120 hrs.	Greater decomposition	Many bacteria
Corium soaked in sterile H_2O at 37° C. for 24 hrs.	Some decomposition	Many bacteria
Corium soaked in sterile H_2O at 37° C. for 48 hrs.	Much decomposition	Many bacteria
Corium soaked in sterile H_2O at 55° C. for 24 hrs.	Much decomposition	Many bacteria
Corium soaked in sterile H_2O at 55° C. for 48 hrs.	Extreme decomposition	Many bacteria

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2. *Physical Conditions.*—The effect of temperature on the growth and activity of bacteria of hide is important. This is shown in Tables VI and VII and is illustrated in Fig. 4.

It is evident from Tables VI and VII that bacterial growth and hence bacterial action is slow at low temperatures and increases with rise in temperature.

3. *The Reaction of the Environment.*—It is well known that the action of enzymes is greatly influenced by the reaction of their environment. Therefore, the reaction of the media should affect the action of both the proteolytic and non-proteolytic bacteria. That this is so is shown in Table VIII.

TABLE VIII.

Conditions	Results after 72 hours at 25° C.	
	Condition of hide	Bacterial growth
Piece of whole hide 2½ in. by 4 in. placed in 300 cc. H_2O just alkaline to litmus with $Ca(OH)_2$	Decomposed	Many proteolytic bacteria
Piece of whole hide 2½ in. by 4 in. placed in 300 cc. H_2O just acid to litmus with acetic acid	No decomposition	Few proteolytic, many non-proteolytic bacteria

In studying Table VIII it is apparent that the reaction of the media plays a role in the decomposition of hide; alkaline reaction favoring decomposition, acid reaction retarding or inhibiting it. These experiments are illustrated by Fig. 5.

Fig. 5.—Solution in left-hand bottle just acid to litmus. Solution in right hand bottle just alkaline to litmus.

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5. *The Respiratory Conditions.*—These play an important role in the growth and activity of micro-organisms, as shown by the following experiments.

EXPERIMENT I.

Two tubes of coagulated blood serum were inoculated with a member of the proteous group. One tube was placed under anaerobic conditions by means of pyrogallic acid and alkali, the other left aerobic; both were then incubated for 24 hours at 37° C. At the end of the incubation period the anaerobic was undigested, while the aerobic was completely digested. This experiment is shown in Figure 6.

Fig 6.—Left hand tube incubated anaerobically. Right hand tube incubated aerobically.

EXPERIMENT II.

Tubes of coagulated blood serum were inoculated with strain No. 6, a member of the proteous group, which is a facultative organism, or which, in other words, grows under both anaerobic and aerobic conditions. These cultures were incubated at 37° C. with the results shown in Table IX.

TABLE IX.

Gaseous environment	Result in terms of digested serum
Aerobic	Very much digested
O_2	Much digested
Anaerobic by pyrogallic acid	No digestion
Aerobic + alkali on cotton stopper (sealed)	Much digestion
CO_2	Slight digestion
H_2	Fair digestion

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It will be seen that the serum was digested best under aerobic conditions; that either the removal of small traces of CO_2 or the addition of large quantities interfered with digestion, and that digestion will occur in the absence of O_2 provided a trace of CO_2 is present.

EXPERIMENT III.

Cultures from water in which a hide had decomposed, were made in 6 tubes of coagulated blood serum and incubated at 37° C. under the conditions noted and with the results shown in Table X.

TABLE X.

Environment	Results in terms of digestion
Aerobic	Fair digestion
Aerobic + alkali on stopper (sealed)	Slight digestion
O_2	Much digestion
H_2	Slight digestion
CO_2	No digestion
Pyrogallic acid and alkali	No digestion

Here it will be seen that mixed cultures digest blood serum under the same conditions as shown in Experiment II.

EXPERIMENT IV.

Pieces of uncleaned hide were placed in 250 cc. of water and kept at 25° C. under the conditions, and with the results shown in Table XI.

TABLE XI.

Environment—48 hrs. soak	Decomposition of hide	Proteolytic growth from solution
Hide in water	Fair decomposition	Fair
Hide in water with O_2 passed through	Much decomposition	Large
Hide in water with CO_2 passed through	No decomposition	Small
Hide in water + 3 per cent dextrose with O_2 passed through	No decomposition	Fair
Hide in water + 3 per cent dextrose with CO_2 passed through	No decomposition	None

Here it will be seen that mixed cultures cause hide digestion under the same conditions as when they digest blood serum. It

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is interesting to note that quite a number of proteolytic bacteria grew in the culture containing dextrose which had oxygen passed through the solution. Part of this series is shown in Figure 7.

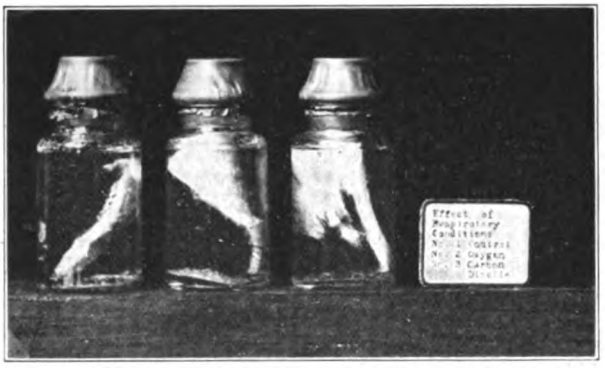

Fig. 7.—Hide shown at left stood in water.
Hide shown in middle stood in water + continuous stream of O_2.
Hide shown at right stood in water + continuous stream of CO_2.

At this point, it is important to note that certain bacteria *e. g.*, members of the Bacillus subtilis group, which are very common inhabitants of hides and are active in their decomposition, grow only aerobically and that anaerobic conditions will interfere with their activity.

Summary and Conclusions

A fresh hide contains many bacteria. These bacteria vary in their morphology, in their biological characteristics and in their action upon hide. Various conditions and factors govern their activity.

The factors which favor bacterial decomposition of hide are: proteolytic bacteria, the presence of protein substances such as blood, a slightly alkaline reaction of the environment, a warm temperature, and the presence of O_2, and small traces of CO_2.

On the other hand, the factors which tend to prevent the bacterial decomposition of the hide, are: the absence of proteolytic bacteria and the presence of non-proteolytic bacteria; acidity; the presence of fermentable carbohydrates, lack of proteins; a low temperature; the presence of large excess of CO_2 and an absence of O_2.

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THE DIRECT MEASUREMENT OF THE PLUMPING POWER OF TAN LIQUORS—1922 COMMITTEE REPORT

V. J. Mlejnek, Chairman

A preliminary letter was sent to all the members of the Committee September 26th, suggesting a line of work to be followed and calling for suggestions and criticisms. On February 1st, directions for the following proposed line of study were sent out:

"Enclosed you will find directions for the first stage of the work to be done by the Committee on 'Plumping.' Samples of commercial lactic acid 22 per cent, ordinary solid quebracho extract 75 per cent tannin, liquid oak bark extract 26 per cent tannin, calcium acetate C. P., and synthetic tanning material are being sent you under separate cover. For acetic acid use J. T. Baker's or Baker & Adamson's Glacial C. P. The first step is a comparison through a set of tests of Claflin's method with a method proposed by Mr. H. C. Reed. It is claimed that the Reed method is distinctly superior to the Claflin method, especially in manipulation, and it seems to your chairman very much worth consideration The two methods are outlined below.

"*Claflin Method*:—Weigh 10 grs. air dry 1921 hide powder into a shaker bottle, pour the prepared liquor from a graduated flask onto the powder, stopper, shake for ten minutes at 60 revolutions per minute as in the determination of non-tannin in a tannin analysis. For filtering use a funnel, capable of holding the whole solution, preferably one with a one-half inch stem bore, the neck of which has been firmly plugged with one-half gr. of absorbent cotton, wet and allowed to drain. At the end of the period of shaking, immediately pour the contents of the bottle into the funnel and collect the filtrate in a graduated cylinder. Rinse out the shaker bottle with some of the filtered liquor and return rinsings to funnel. At the end of 40 minutes or when dripping has ceased, read off volume of filtrate.

"*Reed Method*:—For a description of the apparatus for this method see This JOURNAL, **17**, 112 (1922).

EXPERIMENTAL WORK

"*Standard Solutions*:—Make up the following standard solutions to be used in the experimental work. Dilute amounts given below to 250 cc. with distilled water.

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100	Grs. lactic acid	= molar
15	Grs. acetic	= molar
19.8	Grs. calcium acetate	= half molar
16.8	Grs. ord. sol. quebracho	= 5 per cent tannin
48.0	Grs. oak bark extract	= 5 per cent tannin
50	Grs. syntan	= 20 per cent solution

"Test the following dilutions of the above solutions by both the Claflin and Reed methods, making amounts indicated below up to 200 cc. volume with distilled water and follow the procedures outlined.

5 Cc. and 15 cc. molar lactic acid
5 Cc. and 15 cc. molar acetic acid
5 Cc. and 15 cc. half molar Ca acetate
20 Cc. and 80 cc. queb. = ½-2 per cent tannin
20 Cc. and 80 cc. oak = ½-2 per cent tannin
5 Cc. and 20 cc. syntan = ½-2 per cent solution

"Make duplicate blank determination using distilled water. Note temperature of room.

"That the work may proceed as rapidly as possible, your early report will be greatly appreciated. In your report indicate which method you deem superior and why.

"That some method of expressing the plumping power may be found, you are urged to suggest what you consider the simplest and most intelligible method of expression."

Table showing the plumping values of the various solutions, each man's results being figured on the basis of his own H_2O blank.

As will be noticed in the table, results are fairly consistent when solutions within reason are examined.

The 20 cc. syntan solution is extraordinary in its action, its plumping action being very rapid on the hide and results are rather unsteady.

The members who collaborated in the work were:—

R. E. Porter—Ashland Leather Co., Ashland, Ky.

C. W. Beebe—Kullman, Salz & Co., Benicia, Cal.

F. F. Marshall—Kistler Leather Co., Lock Haven, Pa.

C. R. Oberfell—J. H. Heald & Co., Lynchburg, Va.

G. V. Downing—L. M. Whitmore, Leas & McVitty, Inc., Salem, Va.

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TABLE I.—Cc. Absorbed by Hide Powder

Claflin Method

		Porter	Beebe ‡	Marshall	Oberfell	Mlejnek	Downing *	Blackadder	Average
Lactic	5	107	100	121	107	110	110	99	108
	15	121	128	138	120	126	130	121	126
Acetic	5	81	81	95	81	85	88	81	84
	15	111	94	119	104	107	119	109	109
Ca acetate	5	49	55	70	54	57	55	53	56
	15	53	50	74	54	59	56	56	57
Queb.	20	70	63	78	60	71	62	67	67
	80	68	97	89	66	79	90	75	81
Oak	20	63	55	71	64	67	82	60	66
	80	61	54	74	58	57	60	61	61
Syntan	5	61	57	78	65	70	61	64	68
	20	77	48	98	90	83	43	82	74
Water blank		53	58	71	54	58	58	54	58
Room temp.		20° C.	19°-22°	20°-23°	25°	20°-22°	23°		

Reed Method

								†	
Lactic	5	106	95	114	109	105	102	27	105
	15	126	122	125	130	126	135	34	127
Acetic	5	78	78	76	74	74	79	24	78
	15	108	93	101	113	110	111	30	106
Ca acetate	5	48	49	58	50	41	48	12	47
	15	49	54	53	47	48	53	13	51
Queb.	20	51	61	54	41	38	52	16	50
	80	40	101	44	36	39	97	8	60
Oak	20	55	51	54	51	50	78	16	57
	80	46	59	63	42	57	54	14	54
Syntan	5	55	56	59	61	63	57	25	59
	20	68	43	87	76	60	72	16	68
Water blank		41	54	49	51	43	48	14	48
Room temp.		17°-20°	19°-20°	20°-23°	24°	20°-22°	16°-23°		

‡ Two hundred revolutions per minute.

* By subtracting cc. hide as reported from 200 cc.

† Not included in average—using 2.3 gr. air dry hide to 100 cc. solution.

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TABLE II.—PLUMPING FIGURE—PER CENT PLUMP USING WATER AS STANDARD 100 PER CENT

		Porter	Beebe	Marshall	Oberfell	Mlejnek	Downing	Blackadder	Average
				Claflin Method					
Lactic	5	201.8	172.4	170.4	198.2	189.7	189.7	183.2	186.5
	15	228.3	220.7	194.4	222.2	217.3	224.2	224.1	218.7
Acetic	5	149.4	139.6	133.8	150	146.6	151.8	150	145.9
	15	209.4	162.1	167.6	192.6	184.5	205.1	201.8	189
Ca acetate	5	92.5	94.8	98.6	100	98.3	94.8	98.2	96.7
	15	100	86.2	104.2	100	101.7	96.7	103.7	98.9
Queb.	20	132	108.6	109.8	111.1	122.5	106.9	124.1	116.4
	80	128.3	167.3	125.3	122.2	136.2	155.2	138.9	139.1
Oak	20	118.9	94.8	100	118.5	115.5	141.4	111.1	114.3
	80	115.1	93.1	104.2	107.4	123.7	103.5	112.9	108.6
Syntan	5	115.1	98.3	100.8	120.3	120.7	105.2	118.5	112.6
	20	145.3	82.8	138	165.6	143.1	74.2	151.8	128.8
Water blank		100	100	100	100	100	100	100	100
				Reed Method					
Lactic	5	258.5	175.9	232.7	213.7	244.2	212.5	193	222.9
	15	307.3	225.9	255.1	254.9	293	281.2	243	269.6
Acetic	5	190.2	144.4	155.1	164.7	172	164.6	171	155.2
	15	104.8	172.2	206.1	221.6	255.8	231.3	214	198.6
Ca acetate	5	117	90.7	118.4	98	95.4	100	86	103.3
	15	119.5	100	108.1	92.2	111.6	110.4	93	107
Queb.	20	124.4	112.9	110.3	80.4	88.4	108.3	114	104.1
	80	97.6	187	89.8	70.6	90.7	202.1	57	123
Oak	20	134.2	94.4	110.3	100	116.2	162.5	114	119.6
	80	112.2	109.2	128.5	82.3	132.5	112.6	100	112.9
Syntan	5	134.2	103.7	120.4	119.6	146.5	118.8	179	123.9
	20	165.9	79.6	177.5	149	139.5	150	114	143.6
Water blank		100	100	100	100	100	100	100	100

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T. Blackadder—Reed Laboratories, New York, N. Y.

V. J. Mlejnek—The Graton & Knight Mfg. Co., Worcester, Mass.

COMMENTS OF COLLABORATORS

R. E. PORTER:—Both methods have their advantages and disadvantages. The Claflin method insures uniform and complete agitation, which is very important, but it has the disadvantage that the solution and hide powder must be transferred to more than one container.

The Reed modification involves difficulties in agitation. The percolator cannot be shaken as the cotton pad must be firmly held against the outlet. It is also necessary to let the hide powder and solution stand for some time, preferably over night, in order to insure somewhat complete and uniform plumping.

I prefer the Claflin method as I believe that uniform agitation is all important.

C. W. BEEBE:—In the Claflin method the samples were shaken in an old style shake machine for 10 minutes at a speed of 200 revolutions per minute.

In the Reed method, the liquor was added to the hide powder at 3 P. M., agitated several times until 5 P. M., and then allowed to stand over night.

The Reed method seems to be superior in manipulation to the Claflin method, mainly in there being no necessity of pouring the liquor from the shake bottle to the funnel, and in rinsing the shake bottle. However, standing over night will not permit very close temperature control, which would be an objection to this method.

F. F. MARSHALL:—With reference to the better methods for conducting these tests, find that both the methods give good results, though not comparable with each other, but personally prefer the Claflin method on account of the shorter time required to perform the work.

C. R. OBERFELL:—As to a comparison of the two procedures, I suppose I would prefer to operate the Reed proposal on account of its simplicity, but since the results are considerably different than by the Claflin procedure, I am in doubt as to which gives the more nearly correct results. In other words, this preliminary

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work is quite enough for a start, but it seems to me that considerable more work will be necessary to form an opinion as to the possibilities of the method as a whole and the two variations of Claflin and Reed.

G. V. DOWNING:—*Claflin Method*: This method requires too long to manipulate. The point of getting the right amount of cotton in the point of the funnel is hard to regulate. Some of the tests were dripping after 40 hours. I feel that this method is not suitable.

Reed Method: This method is better, in that there is less manipulation. There is still the time factor that is annoying. Thirty-six hours needed in some cases. The cotton plug was again a difficulty.

A general comment on these two methods would be that the factor of capillarity has too great an influence in the results. If the osmosis factor was the only one present, these two methods would be satisfactory.

Modified J. A. Wilson Method: This was simply the transferring of the swollen hide powder from the Claflin tests to tall graduated cylinders, and the volume of the hide powder was read off after standing over night. The objection to this method is the same as that found in the J. A. Wilson method itself, that there is difficulty in reading this volume accurately.

We tried various means to obviate this, such as trying to weight down the top with a light perforated disk, but without results that were uniformly satisfactory.

I would like to make the following suggestion. How would it work if one were to use a suction flask to draw off the excess acid? My idea would be this: Weigh up ten grams of hide powder, and either shake or allow to stand over night in the solution to be tested. Then pour the mixture of hide powder and liquid into a Gooch or Buchner funnel, using a mat of cotton, asbestos, or even paper, and drawing off the liquid into a graduated cylinder so fitted as to be connected up to a suction. I should think that a moderate suction, applied until the drops stopped would be sufficient. I have no data to present on this method, but I think that it would work.

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T. BLACKADDER:—The Reed method appears to be simpler in execution and more concordant in its results than the Claflin method and we would give it our preference.

From a comparison of the figures I obtained by the two methods, it appears to me that a very important point is brought to light. The action of solutions containing tannin is radically different according to the method used. Is not this due to the different degrees of tannage acquired by the hide In the Reed method, a smaller proportion of hide was employed and the tannage effected by the solution was higher. Thus in the case of the quebracho, which is a low acid material, we find a repressing at the higher concentration, whereas with syntan, which is a highly acid material, we find a swelling which is lowered at the higher concentration. In the Claflin method, the hide was not so thoroughly tanned and acted more like fresh hide.

If one is to draw practical deductions from the analytical data, would it not be better to aim at paralleling the conditions of the yard? In other words, the hide powder should, during the experiment attain a degree of tannage comparable to that existing in the yard in the liquor under investigation. From the results before me, I think this condition is more nearly realized when 2 per cent hide powder is used than when 5 per cent is used.

CHAIRMAN:—Perhaps Downing's difficulty with slow filtration was due to plugging the funnels too firmly. If the cotton plug is put into the neck of the funnel just firmly enough to keep it from slipping when the test liquor is poured onto the funnel, I think the filtration will proceed at a fair rate. His suggestion of applying suction seems to have the undesirable feature that the suction is apt to draw some of the water right out of the plumped hide, and a variation in pressure would only vary the error.

As Porter says, there is difficulty in getting proper agitation when using the Reed method, and proper mixing of hide and liquor is an important factor. Temperature variation during the over-night contact of hide and liquor seems a rather important possible source of error unless blank determinations are made with each set of tests. I understand that Mr. Reed himself has abandoned the method as impractical, and has replaced it with a different one.

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Too late for any tests in Committee work, the suggestion was made that the hide powder be wet thoroughly before testing the liquors, thus bringing it back to a state more comparable with actual tannery practice, and at the same time avoiding any possible case-hardening effect of strong liquors on the hide. I have tried this out and am convinced that better results will be obtained.

The Claflin idea, namely, of using hide powder to determine the plumping power of liquors, appeals to me as the best so far. The procedure will undoubtedly be improved by first wetting the hide powder, and by allowing the "hide-liquor" to stand some time before filtering. Possibly the amount of hide can be cut down without sacrificing accuracy. At any rate, the Chairman believes that more work should be done along this line and recommends that the Committee be continued another year for this purpose.

NOTE ON THE WILSON-KERN METHOD OF TANNIN ANALYSIS

By G. W. Schultz

Received June 9, 1922

Up to the present time all of the data presented on the Wilson-Kern method for the determination of tannin has been given by the authors of the method and by the writer. One set of results have been directly contradictory to the other. One point at issue between the authors of the method and the writer has been the matter of concordance and the ability to obtain results that check each other for the same material. The writer has presented results[1] on the same extract which showed a very wide variation and has cited some causes for such a variation, some of which are backed by experimental evidence. All of this is briefly dismissed by Wilson and Kern by attributing the erratic results to a lack of skill or equipment. At the same time they claim that unskilled help in their laboratory obtain excellent check results. The concentration and time factors are considered to have no effect on the amount of tannin combined with the hide powder and these factors are considered to be adequately taken care of when it is stipulated that a solution of tannin be used of

[1] This Jour. 15, 654; 16, 349 and 637.

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such strength that after shaking with the specified amount of hide powder for 6 hours the filtrate gives no precipitate with gelatin-salt reagent.

In a recent paper by Thomas and Kelly[2] there are sufficient data given to corroborate the claim of the writer and to show that for at least two reasons the Wilson-Kern method does not fulfill the affirmations that have been made for it. Thomas and Kelly conducted their work by adding 200 cc. of solutions of gambier and quebracho extracts of varying concentrations to 10 grams of absolutely dry hide powder in a 400 cc. rubber-stoppered bottle and rotating for the desired time. The filtrate was tested with gelatin-salt solution in each case. The tanned hide powders were then "washed with running water and transferred back to the bottle, covered with 300 cc. of water, tumbled for 0.5 hour, and filtered again. This washing operation was repeated until the filtrate no longer showed a dark color upon addition of a few drops of ferric chloride solution." The washed, tanned hide powders were squeezed out, dried in a current of warm air and analyzed for moisture, nitrogen, matter extracted by chloroform and ash. The tannin was determined by subtracting the sum of these from 100. The following data are taken from that presented by Thomas and Kelly. The per cent of tannin in the extract is computed for each case on the assumption that 10 grams of absolutely dry hide powder is equal to 10 grams of hide substance which makes the results for per cent of tannin in the extract higher than if the true value were used but, nevertheless, the difference is relative.

Here we have exhibited a striking paradox—one and the same extract in each case has two and more values for its true tannin content. In the case of gambier for the six-hour period it is stated that the solution having a concentration of 25 grams of extract to 1 liter gives a filtrate that gives no indication of tannin; the solution having a concentration of 60 grams per liter evidently gives a faint trace; and the solution having 100 grams per liter gives a positive reaction for tannin. Now, according to the calculations, the values for per cent of tannin in the extract are 2.78, 5.16 and 3.29 per cent respectively. It is seen that the last

[2] Time and Concentration Factors in the Combination of Tannin with Hide Substance, *J. Ind. Chem. Eng.*, 14, 292 (1922).

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Gambier Extract

Time of shaking		6 hours			72 hours			2 weeks	
Concentration of solution in grams extract per liter		25	60	100	25	60	100	*60	*100
Reaction of filtrate to gelatin-salt test		–	Practically –	+	–	–	+	–	Slightly +
Tanned hide	H. substance per cent	83.66	80.30	83.01	87.61	83.17	81.29	75.31	76.09
	Tannin (by diff.) per cent	1.16	4.97	5.45	1.76	4.78	5.99	5.36	6.88
	Tannin / 100 H. S.	1.39	6.19	6.57	2.01	5.75	7.37	7.12	9.04
Per cent tannin in extract		2.78	5.16	3.29	4.02	4.79	3.69	6.35	4.84
No. of washings received by powder		9	12	30	18	35	60	11	43

Quebracho

Time of shaking		6 hours			72 hours			2 weeks	
Concentration of solution in grams extract per liter		6.3	17.0	35.0	6.3	17.0	35.0	*17.0	*35.0
Reaction of filtrate to gelatin-salt test		–	–	+	–	–	Slightly +	–	
Tanned hide	H. substance per cent	80.50	72.88	68.92	78.49	71.53	69.77	71.03	67.82
	Tannin (by diff.) per cent	3.24	10.46	15.41	3.09	11.03	16.71	10.60	16.42
	Tannin / 100 H. S.	4.03	14.35	22.36	3.94	15.42	23.95	14.92	24.21
Per cent tannin in extract		32.0	42.21	31.94	31.27	48.30	34.23	45.40	35.79
No. of washings received by powder		11	11	44	18	18	60	11	42

* The concentrations were slightly different in this case but it has been taken into consideration in the calculation.

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solution gives a higher value than the first in spite of the fact that the former gives indication that all of the tannin is not removed from the solution in the tanning operation. The second solution exhibits a similar state of affairs, only more so, as it gives a higher value for tannin in the extract than either the first or third solution. The same solutions give a different value for per cent of tannin upon prolonging the time of tanning. Thus we obtain almost any value, for the per cent of tannin in the pasty gambier extract used, between 2.78 per cent and 6.35 per cent. The same is true of the quebracho with tannin values between 31.27 per cent and 48.30 per cent.

The work of Thomas and Kelly[3] from which these data are taken is based on the postulates on which the Wilson-Kern method of tannin analysis is based and for this reason the work can have no value. The ferric chloride test is taken as a positive indication of the presence of non-tannins but it is not, as pure tannin in dilute solutions will give the same reaction as the non-tannins. In spite of the statement to the contrary there is a great deal of evidence to support the belief that a portion, at least, of the tannin removed from solution by hide powder is removed again by washing the tanned powder with water. Whether it is a case of reversible adsorption or hydrolytic decomposition or a combination of the two may remain an open question. These results could be taken as an indication of the amount of tannin which is more or less firmly combined with the hide powder under the conditions given were it not for the fact that the methods used presented many possible sources of error[4] all of which would make us accept such results with extreme caution.

The unquestioned acceptance of the hypotheses of Wilson and Kern is the only novel part of this investigation. As early as 1892 J. Von Schroeder and J. Paessler[5] published the results of an investigation which was concerned with the effect of concentration on the amount of tannin absorbed by hide. These investigators arrived at the conclusion that with increasing concentration of tannin in liquors there is an increase in the amount of tannin absorbed by hide up to a maximum, then a decrease to

[3] *loc. cit.*

[4] This Jour. 16, 349 and 637 (1921).

[5] Absorption of Tannin by Hide, *Dingl. Polyt. Jour.*, 1892, 284, 256 and

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a minimum when a further increase in concentration of the liquor causes no change. They explained the fact that the hide absorbed less from the stronger solutions by the assumption that tanning with the stronger solutions is only superficial and that the surface of the hide particles is so completely tanned as to prevent penetration of the tannin into the interior. These investigators found that 100 parts of hide powder at its maximum point of absorption took up about 83 parts of tannin.

Recently Moeller[6] investigated this assumption and after extensive experimentation arrived at the conclusion that it was true up to the point where it needed a little elaboration to take into consideration the time factor. This investigator considers that the fact that such a coating action is obtained with the stronger solutions and not in the weaker solutions is due to a difference in degree of dispersion of the tannin in such solutions. In the lesser concentrations the tannin particles are very fine and penetrate the hide more easily than the coarser particles in the stronger solutions. The writer maintains that a similar assumption offers a more plausible explanation of the effect, termed astringency, than that offered by Wilson which Thomas and Kelly cite. This work by Thomas and Kelly in common with the work of the other investigators mentioned was conducted by introducing *air dry* hide powder into the tannin solutions and it is very difficult to see what light such a procedure can throw upon the practice of tanning. The hide which goes into a tanning liquor in practice does so with a water content of 70 to 80 per cent and the desirability of having it so has been recognized since the beginning of tanning hides in aqueous solutions. The result that would be obtained by introducing a dry hide into a tanning liquor is common knowledge to all tanners some of whom have no knowledge of chemistry, why should it be less so with the chemist who should know what occurs when one tries to conduct a reaction to completion with an aqueous solution of one of the reactants and a dry mass of the other, especially when the product of the reaction is insoluble or nearly so.

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[6] Researches on the Processes of Tanning. *Ledertechn. Rund.* 12, 89 (1920), et seq.

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DISEASES OF THE FRENCH CHESTNUT TREE— PARTICULARLY THE "INK-MALADY" *

By E. Schell

President of the Society of Leather Trades' Chemists

Our chestnut forests offer to parasitologists and cryptogamists one of the greatest fields for exploration. One knows of the long life of our chestnut trees, extending often into several centuries, and that this beautiful tree, during its entire life from youth to old age is subjected to the attack of numerous injurious animal and vegetable parasites. Few plants are so capable of sheltering so many useless and harmful inhabitants. Fortunately many of these are inoffensive and but slightly injurious. We will deal, therefore, only with those which cause serious damage.

The nut is frequently attacked by the worm, *Carpocapsa splendana*, and two fungi, one the *Penicillium glaucum*, which causes the *blue rot*, and the other, *Aspergillus niger*, causing a yellowish-black hardening, which imparts to this excellent fruit an intolerable taste. These three parasites of the nut cause annually a loss of nearly one-third of the crop. Let us add that recently an eminent Italian, B. Peyronel, attributes the cause of the black rot of the nut to a *hyphomycete*, the *Racodiella castaneae*, from which he appeared to obtain by culture the ascophore form; this fungus would seem to be a discomycete of the genus *Sclerotinia*, which he believes identical with the *Sclerotinia pseudotuberosa, Rehm*, from the acorn of the oak, which is extremely polymorphous, particularly in its vegetative organs.

The young leaves readily become the feeding ground for a caterpillar, *Phigallia philosaria*, which appears, however, to have completely disappeared from certain regions. During wet years the leaves of the chestnut frequently are covered in August and September with a yellowish netting, causing them to fall. These fallen leaves are peppered with brown stains. This disease appears also to reflect its effect upon the fruit, making the nuts small and imperfect.

Concerning the wood, the fungus *Diplodina castaneae* dries up the young saplings and renders them unfit for cutting. Another fungus, a *Coryneum*, attacks the large and small branches, which it kills. This fungus also plays its part in the diseases of the

* Translation by R. W. Frey Rend at the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Canada, June 23, 1922.

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roots as we shall see later. On the trunk of old chestnut trees the enormous flat larvae of triangular outline with the large horned head of the *Capricorne cerambix, Heros,* bury into the wood near the bark in long, flat galleries 5 to 6 centimeters wide, and are capable of causing the death of the trees. When the insect is established in the forest it multiplies rapidly, even though its larvae require four years to develop into the perfect insect.

Among the diseases of the roots of the chestnut tree let us cite first the old rot caused by the *Agaricus melleus,* a large fungus not specific to the chestnut, and which kills many other trees on calcareous soil, as the mulberry for example. Its centers of infection generally of slight consequence, are at first active and then lie dormant some years, often dying out spontaneously. It is easy to recognize the great tufts of *Champignons a collerette,* which appear, generally in the autumn, at the collar of dead trees. Its mycelium is violet white and phosphorescent in the dark, forming continuous plates between the bark and the wood of the root or base of the trunk. The *Agaricus melleus* has always existed in our chestnut forests, as also the *Hypholoma fasciculare,* which grows likewise in large, greenish-yellow tufts on diseased bases. This saprophyte common to all decaying roots, is characterized by a golden yellow mycelium interlacing the roots.

We will take up now in detail the terrible "ink malady" which has completely ravaged the chestnut forests of the Pyrenees, menaced many other regions, and caused much alarm to the public authorities and private interests. In treating of this subject we can not do better than refer to the report made in 1918 to the Sub-committee of Ardèche on Conservation by our distinguished mycologist and renowned hybridist, G. Couderc, of Aubenas near Vals, who is studying this particular disease and remedies for the same in an isolated nursery.

General Characteristics of the "Ink Malady"

The first outward symptoms which one can notice are in the spring when the male catkins do not open and fall without having blossomed; the chestnuts are then generally rare and always very small.

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Still more characteristic is the second stage with an intense yellowing of the leaves in July, these leaves being besides smaller than normally. This yellowing enables one to locate from afar a chestnut forest which has been attacked and to define the extent of the disease, the effects of which spread out toward the edge of the forest in a manner suggesting an oil stain, and in such fashion that one can estimate the center of the original invasion where the trees have disappeared. When the diseased trees have turned yellow in July, they may die rapidly, as soon as within two years, if on poor and uncultivated ground and somewhat slower on rich, fertilized soil, but do not survive for more than 4 to 5 years. The young shoots from the foot of trees killed by this disease have generally very little vigor, they never bear fruit and quickly die as soon as one of their roots is attacked by the disease and in turn rots.

The really essential characteristic of this disease is the rotting of the roots, a rot which comes from the depth of the soil. The disease undoubtedly arises from considerable depth and follows one or more roots. The soil beginning 40 centimeters from the surface becomes thus a deadly medium for the young tree which starts either as a seedling or from setting out. If before replanting one should dig up the infected earth for a depth of 70 to 80 centimeters, the replanted chestnut trees grow at first with extraordinary vigor, but no matter how vigorous they may be, they die towards their fourth or fifth year and upon examination it will be found that the taproot or one or more large roots have rotted.

Finally, the characteristic from which the "Ink Malady" draws its name is a violet black or yellowish-black exudation at the base and largest roots; this exudation blackens the surrounding soil and stones for a distance of 6 to 7 centimeters or sometimes more. But it is noted that this exudation is not always present and that it appears to depend on the soil and especially the year; the foot of young trees which die suddenly generally show but little, if any, of this particular phenomenon. On the other hand, it is especially the invading and epidemic march of the disease that quickly mows down without interruption, which is characteristic; whereas the chestnut trees which die from the attack of other parasites, such as the *Agaricus melleus*, die singly or successively at intervals of several years.

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Etiology of the "Ink Malady"

The multitude of animal and vegetable parasites and semi-parasites which are found on the healthy chestnut tree, a number which is greater yet on diseased trees, makes very difficult the task of determining the part played by each and of identifying the real cause of the disease. It is certain, however, in all cases, that the disease is caused by a parasite of the root. Naturally one has first of all incriminated the fungi, such as the *Agaricus melleus* and *Hypholoma fasciculare* of which we have spoken and have shown that they can not be the cause of this terrible disease. Delacroix, who has studied the disease at Aubenas, admitted that the constant mycorhizal parasites of the rootlet extremities of cupuliferae have furnished a new parasitic form which destroys the extremes of the rootlets and thus leads to death by suffocation. But Couderc, while recognizing that very vigorous chestnut trees had none, or very few, of the mycorhizal parasites on their rootlet extremities, has declared that these mycorhiza alone never cause the death of the chestnut tree and considers them as semi-parasites, only relatively injurious. The Italian mycologists have admitted as a possible cause a *Coryneum* of which we have spoken above, and which they suspect of descending to the roots to become there a dreaded parasite. But it should be recognized that this *Coryneum* is found to some extent everywhere, killing branches here and there, leading sometimes even to the death of young trees, but never taking the invasive and merciless form of the "Ink Malady." On the whole it is always a harmful parasite and even very injurious in damp and unhealthy soil, but spares, at least generally, the life of the tree and remains in the sporadic form. One has always incriminated without much conviction or decisive proof, all kinds of bacteria which are always resorted to at the end of other arguments. Notable among these is an anaerobic zoogloea bacterium nearly a coccus in form, which is confounded readily enough with certain organs of conservation of fungi of which we will speak further on.

Couderc, from his interesting bibliographic researches, has come to consider the fungus *Mycelophagus castanea, Mangin*, as nearly certain to be the cause of the "Ink Malady." In fact, if one makes a longitudinal cut in the root of a young chestnut tree

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afflicted with the "Ink Malady," it will be observed that the infected part of the root is overrun by an extremely fine mycelium about one micromillimeter in diameter; varicose, colorless, roughened and very branching, with short branches terminating in the interior of the cells in coralloid clusters, appearing to play the role of sucking branches. This mycelium is connected with rhizoids, dirty, yellowish-white upon drying, which run to the surface of the bark, with varicose hyphae that do not appear septate; the coralloid extremities of the mycelium greatly resembling large coccus-form bacteria. Couderc has not succeeded in inducing the fungus to fruit in culture, nor does he share the opinion of Mangin concerning the parasitism of the mycorhiza and indeed doubts that method of invading the roots.

On the other hand from culture in boiled water one observes disseminated in the diseased bark very numerous dark brown sclerotia of very diversified form which appear to be connected with the fine, colorless mycelium; one has not been able to distinguish these sclerotia in nature, it being realized that the sclerotia arising from the mycorhiza are so abundant and confusing. But these sclerotia very probably represent the organs of preservation of the fungus deep in the soil which explains the permanence in the contaminated soils, where one observes no other tree than the chestnut afflicted with the "Ink Malady." This *Mycelophagus castanea, Mangin,* appears, therefore, to be the cause of the disease. It acts as an aerobic or a semi-anaerobic parasite; it can penetrate eventually through the mycorhiza and probably also by some other means; it invades the tissue of the roots from the depth of the soil, traveling there in the usual manner for parasitic fungi. It would appear to be an *Oomycete* but its true organs of fructification are still unknown or doubtful. It is certain that this fungus is best suited in an anaerobic medium for it has been noted that the last chestnut trees to survive the disease are always those on the edge of terraces where their roots are not deeply covered and consequently relatively aerated.

Remedies

Extensive experiments have been made on the application to this disease of treatments analogous to those for grapes, which are attacked in a similarly serious manner by the *Phylloxera.*

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Various insecticides and fungicides with a base of carbon bisulphide have been tried. Mangin has succeeded in sterilizing the soil with sulphate of iron but since the disease extends deeply into the soil and the chestnut trees, unlike grape vines, are planted far apart with the roots running to great depth, it is very difficult to successfully apply the remedy. Couderc has also succeeded in prolonging the life of diseased trees by strongly fumigating them each year with sodium nitrate, but one can see how difficult it would be to apply such treatment in forests.

In consideration of these difficulties one is therefore led to the study of grafting on resistant species such as practiced on the grape vine; and towards the production of hybrids of chestnut and oak, the oak being entirely resistant even in contaminated soil beside diseased chestnut trees. But grafting on different indigenous oaks is difficult and has not given the results expected; it might be well, however, to try grafting on the Algerian oaks with chestnut leaves and on the *Castaneopsis,* the chestnut varieties of India.

Couderc has tried the hybridization of chestnut and oak without success and even should a resistant hybrid stock be found there would remain the difficulty of reproduction which could be accomplished only by the very long process of layering. However, it appears that there exists in Japan numerous hybrid varieties of chestnut; some wild, which become very large trees; others cultivated, which are generally dwarfed and of varying resistance. From this series of Japanese hybrids, Prunet, of the faculty of Toulouse, has already tried at Ande and Charente some seedlings of "Numbo" and "Parago" and de Bournet at Ardeche, the "Tambu." The first two did not seem to offer a resistance as great as that of the "Tambu;" the latter resisting in general the "Ink Malady." They do not appear capable of developing into large trees, but their fruit are nearly the shape and quality of our best nuts.

According to Couderc it would therefore be well to select for soil contaminated with the "Ink Malady" a wild form of Japanese chestnut for development into large trees to serve eventually as graft stock for our beautiful indigenous varieties. But what patience and work this still requires! Furthermore, it is necessary to consider that the Japanese species are subjected to an aerial

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parasitic disease of the trunk and branches from the *Endothia parasitica*, a disease without importance in Japan but susceptible of becoming in other climates, as the United States for example, a plague more serious even than the "Ink Malady."

Briefly, such is our actual knowledge of this terrible disease which menaces our rich forests and for which, after all, we do not have the necessary effective and practical remedies.

BOOK NOTICES

PRACTICAL TANNING. By Allen Rogers. Partly based on the Third Edition of "Practical Tanning" by Louis A. Flemming. 699 pages with 124 illustrations. Henry Carey Baird & Co., Inc., New York. Price $10.00.

A treatise covering the modern processes as applied in the manufacture of leather and allied products is truly a formidable undertaking and such is the declared purpose of this volume. The subjects range from the classification, flaying, curing and disinfection of hides and skins through the different methods employed for the several operations employed for preparing hides and skins for raw hide, oil, alum, chrome, iron, vegetable and combination tannages, with a varieties of processes for each kind of tannage, to the disposal of tannery wastes. Chapters are devoted to the manufacture of light leathers, sole, belting, strap, welting, etc., and patent leathers, dyeing of leather, fat-liquoring, finishing leather, wool skins and furs, vegetable tanning materials—their preparation for several modes of leaching and the manufacture of extracts, synthetic tanning materials, unusual tanning processes, artificial leather and leather finishes, analytical methods, and useful data. The treatment of such an array of subjects cannot be exhaustive in a book of this size hence omissions and the lack of considerable detail are to be expected. This book is an improvement over the volume of the same name by Flemming and as a source of general information must be of considerable value to both the practical tanner and the leather chemist.

In the preface the author declares that this book, "being intended primarily for those interested in the actual production of leather, deals with the subject from the practical rather than from the theoretical standpoint" which implies that theory has little interest in the actual production of leather and is difficult to understand when we consider its source. It is the reviewer's opinion that many of the subjects treated in this book are greatly in need of a little theoretical treatment and that it is unfortunately lacking. Some of the processes given, which the writer assumes the author has described because they are common practice among tanners, do not conform to theory nor good practice and sadly show the need of chemical direction. As a single example, the several processes described for two-bath chrome tannages may be taken. The majority of these processes described are identical with Schultz's original formula and

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the remainder do not differ greatly from it. Theory shows us that the proportion of acid to bichromate in the first bath is much too low for the complete liberation of the chromic acid and practice along this line has resulted in considerable economy. The chemist, who in spite of the author's inference to the contrary, is vitally interested in the practice of tanning, will find much of interest and much with which he will disagree such as the statement that hydrochloric acid is safer than sulfuric acid for deliming.

It appears in several places as if the author were confused on the subject of the two tanning materials, oak-bark extract and chestnut wood extract. On page 265 we have the statement—"True oak-bark tannage is practically a thing of the past, and what is sold as oak is in reality chestnut oak." While the statement may be true, still the chestnut oak is an oak and its bark yields a tanning material that has all of the tanning characteristics of any known oak-bark extract. In the description of union tannage the extract blend is given several times as a mixture of chestnut wood, chestnut bark and hemlock bark extracts. In the discussion of tanning agents used for belting leather we are told that the basic material should be chestnut-oak wood and in the same paragraph chestnut-oak wood and chestnut wood are used as if they were synonymous. Although the use of the term chestnut-oak wood predominates the author must mean chestnut wood. We are told that "the best chestnut-oak wood is not only cheap, but it is practically inexhaustible, in view of the fact that it requires only 20 years for a chestnut tree to grow to a size at which it may be cut." So far as the reviewer is aware, there is but little, if any chestnut-oak wood extract produced and no chestnut bark extract.

In a chapter of some 79 pages on analytical methods the author has assembled methods of testing the great variety of materials used in leather manufacture, among which is included the official and provisional methods of the A. L. C. A.

The print and paper are excellent and the workmanship good. As a whole this book is worth the price to those interested.

G. W. S.

PFLANZLICHE GERBMITTEL UND DEREN EXTRAKTE. (Vegetable Tanning Materials and Their Extracts). By Josef Jettmar. 216 pages with 33 figures. A. Hartleben's Verlag, Vienna. Price 48 marks.

The treatise is unquestionably the best of its kind that has appeared up to the present time. It is divided into five sections. The first is an excellent resumé of the present state of our knowledge on the questions of the physiological functions and chemistry of the tannins. The second is a treatment of the analytical investigation of tanning materials including sampling. qualitative investigation and quantitative determination. The third section is confined to the description of the individual tanning materials and their extracts. This includes 20 materials as follows: Oak, pine, mimosa, mangrove, maletto and willow barks; valonea, myrobalans, algarobilla, bablah, divi-divi, galls and knoppern; oak, chestnut and que-

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bracho woods; catechu, gambier, sumac, canaigre and palmetto. The author has endeavored to describe the nature and characteristics of each of these materials so far as they are of inportance to tanning practice in Central Europe. The fourth section treats of the manufacture of extracts and the fifth is a bibliography.

The author's German is simple and clear and does not require an extensive familiarity with German to read. The only real criticism of this book is to be directed at the poor quality of the paper and the use of German letters. Although the printing is clear the use of Roman letters would be welcomed by many readers.

G. W. S.

ABSTRACTS

A New Conception of the Generation of Vegetable Tannins. By E. SCHELL. *Le Cuir*, 11, 120, 1922. The recent work of Moureu and Dufraisse may add considerable to our general conception of the origin and significance of vegetable tannins. From their experiments with phenols and polyphenols, substances which are so intimately related to our vegetable tannins, they have demonstrated that spontaneous auto-oxidation of a large number of substances can be prevented by very small quantities of those phenols which they designate as anti-oxidizers. Among the most active of these are pyrocatechin, hydroquinone, and pyrogallol. Ordinary phenol and resorcinol are but slightly active and phloroglucin on the contrary accelerates auto-oxidation. Experiments showed that the action of certain phenols upon aldehydes, such as acrolein, was considerable. Hydroquinonc appeared to prevent any oxidation of acrolein in proportions as small as 1 part in 20,000 and even 1 part per million showed a definite retarding action. Experiments over several years showed that the inhibiting effect was very lasting and furthermore the added phenol was largely recovered unaltered. Its action does not appear to be rapidly diminished and suggests one of catalytic nature. In addition to fixation of oxygen, auto-oxidizable substances often show certain secondary reactions generally of condensation which is evidenced by changes such as in color, viscosity, hardness, rancidity and so on. The preservative phenols likewise retard these secondary reactions. It may therefore well be that the polyphenols so frequently encountered in the vegetable kingdom play there the role of protective agent against too rapid oxidation and that by this metabolism of plant life they are transformed partially into condensation products which are our vegetable tannins.

R. W. F.

The Cattle Pest (Rinderpest). By L. PANISSET. *Halle aux Cuirs*, Mar. 19, 1922, 65-74. The wide spread distribution of the cattle pest or plague with the symptoms of the disease and means of combating it are discussed. The cause of the disease has not been identified but it is conceded as due to a specific virus. The disease spreads rapidly at times

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and on the average the mortality rate is about 75 per cent although it varies according to the epidemic and breeds. The blood of animals having the disease is very pathogenic, inoculation with 0,001 cc. being sufficient to reproduce the malady. The urine, tears and secretions of stricken animals also contain the germs. The virus of cattle pest is rapidly destroyed by dessication, heating, or antiseptics, a point of importance, since with proper handling dried hides, manes, horns and wool from infected countries need not be feared as sources of the disease.

Means of combating the disease vary according to conditions in the country and whether the outbreak is from sudden invasion or permanent infection. Sanitary measures are rarely effective except in countries possessing excellent sanitary organizations. Quarantining of introduced animals does not guarantee the freedom from infection that one would desire. The only certain way to protect a country free from the disease is to forbid entrance of all animals and products which may come from infected areas. Vaccination which has for its object protection of the animals by giving them a slight attack does not give good results. In South Africa and Europe vaccination is sometimes done with bile from animals which have died from the disease. As a result of this 30 per cent of the animals treated may die.

Serum, from animals which have withstood a first attack of the disease, after being treated with virulent blood, has both preventive and curative properties. The serum injections however afford protection for a short time only. For more permanent immunity it is necessary to inject a small quantity of the virulent blood with the serum. This process of sero-vaccination in use in Indo-China should be carefully followed. It involves some risk of giving the disease and experience only will show if its real advantages more than compensate its disadvantages.

R. W. F.

Stains in Dyeing Glove Leather. By A. Rigot. *Halle aux Cuirs*, March 19, 1922, 81-86. In dyeing glove leathers in grays and medium colors certain very serious stains or marbled effects often occur without any apparent cause. The stains show up after dyeing skins which when selected in the white state were apparently perfect. To avoid these stains it is necessary, after purging the skins, to see that they do not come in contact with any other solutions untill ready for dyeing. Skins prepared in different lots should not be mixed nor even placed in contact with one another for very long, a point which requires close supervision in those cases where the skins are prepared one day for dyeing the next. Other stains somewhat similar to the above but occurring much less frequently and on light shades have been demonstrated as due to exposure to ammonia fumes from the mordants being used.

R. W. F.

A Note on Catechu Gambier. By M. J. Zublerv. *Bull. soc. ind. de Mulhouse*, June 21, 279 (1921); *Le Cuir*, 11, 131 (1922). In loading silk with tin and gambier extract, it is found that the purer extracts of gambier made with modern equipment give yields decidedly lower than

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obtained with the native extracts made in the old way in an open vessel. Even the latter show large losses due to the fact that the catechin has but little affinity for silk impregnated with tin which reacts mainly with the non-crystalline catechu-tannic acid portion of the extract. Catechin at first actually may cause a loss of tin but upon using the bath of catechin extract a second time a noticeable increase in weight is obtained showing that the catechin has undergone a transformation rendering it capable of forming a lake with the tin. By boiling pure catechin a decided increase in yield is obtained but on the contrary boiling catechu-tannic acid gives a lower yield. A mixture of pure catechin and catechu-tannic acid gives results analogous to gambier and it can be realized therefore what effect heating gambier extract in the open has from the viewpoint of weighting silk. There are certain reactions between the catechu-tannic acid and catechin. With the Chinese gambier containing altered catechin, boiling gives superior yields. By more or less prolonged heating of gambier extract the catechin can be changed so as to be taken up by silk loaded with tin.

R. W. F.

The Influence of Formaldehyde on the Adsorption of Tannin by Animal Skins. By O. Gerngross and H. Roser. *Coll.*, **621**, 1–13 (1922). Formaldehyde has been found to decrease the amount of acid adsorbed by hide powder so it was of interest to study the effect of formaldehyde on the adsorption of vegetable tannins, especially since formaldehyde is often used in the preparation of the hide for tanning or to hasten the tannage. Three samples of hide powder which had been treated with (I) no formaldehyde, (II) a small amount, (III) a large amount of formaldehyde, were used. Before use the acidity of samples (I) and (III) was adjusted with hydrochloric acid to that of sample (II). Portions of each hide powder, containing 0.5 gram of the dry substance, were treated with 100 cc. portions of tannin solutions of ten different strengths (ranging from 0.85 to 8.5 grams per liter) and allowed to stand for 4, 48 and 168 hours. The tannin remaining in solution was then determined by the Schroeder-Löwenthal method, which was found by a preliminary investigation to be accurate within 1 per cent for solutions containing less than 1 per cent tannin. In all cases it was found that the adsorption of tannin decreased as the formaldehyde tannage increased. With untreated hide powder the adsorption followed the Freundlich isotherm, reaching equilibrium in about 2 days, but with the treated hide powder the adsorption was more irregular and there was evidence of saturation in the most concentrated tannin solutions. A comparison was also made of the adsorption of tannin by formaldehyde leather and unhaired skins which had not been treated with formaldehyde. The former not only absorbed less tannin than the latter but in no case was the rate of adsorption of the tannin increased by the formaldehyde. Formaldehyde should therefore be used with care in tanning.

I. D. C.

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The Influence of Pre-treatment with Formaldehyde on the Ability of White Analytical Hide Powder to Adsorb Vegetable Tannins. By O. Gerngross and H. Roser. *Coll*, 622, 28-30, (1922). The quantity of a technical tannin adsorbed by hide powder was found to be decreased if the hide powder had been treated with formaldehyde, just as was found to be the case with tannin (*Coll.* 621, 1, 1922). Portions of an oak-wood extract of the usual strength, containing 4 grams of tannin per liter, were treated by the prescribed method with 6.5 gram portions of the three hide powders used previously. Although an excess of hide powder was present the formaldehyde tanned powders did not detannize the solutions. With gelatine-salt solution the non-tannin solution from hide powder I gave a clear solution, that from hide powder II gave an opalescent solution and that from hide powder III gave a very cloudy solution.

Hide powder		Resistance to boiling water	Tannin	Non-tannin
Not tanned with formaldehyde	I	5.2	19.77	8.84
Lightly tanned with formaldehyde	II	45.5	18.65	9.96
Strongly tanned with formaldehyde	III	78.7	15 02	13.59

While formaldehyde is useful in preventing bacterial action in the moist hide powder and also in decreasing the solubility of the hide powder, it decreases the power of adsorption to such an extent that its "Resistance to Boiling Water" (the per cent of the ash and moisture free leather not dissolved by boiling water; *Coll.*, 1908, p. 495) should probably not be over 10 or 20. The stability of this hide powder should be investigated for the power of adsorption of strongly chromed hide powder is known to decrease with time, and Parker (*Coll.*, 1906, 404) found that the power of adsorption of a formaldehyde tanned hide powder was very inconstant.

I. D. C.

PATENTS

Tanning. British Patent 174,700. J. Y. Johnson, London.—(*Badische Anilin* and *Soda Fabrik; Ludwigshafen-on-Rhine, Germany*). Oct. 26, 1920, No. 30,276. Hides, skins, etc., are tanned by treatment with aqueous acid solutions of the sulphonated products obtained by condensing a carbohydrate with an aromatic hydrocarbon or carbazole or halogen substitution products thereof, the sulphonic acid groups being introduced either by effecting the condensation in the presence of sulphuric acid or by using a sulphonic acid of the cyclic component as reacting material. Natural vegetable tanning-agents may also be present.

Treating Hides etc., British Patent 175,314. O. Richter, 81, Bradenburg, Germany. Aug. 14, 1920, No. 23,799. Relates to the depilation of hides and skins in closed chambers by the action of heat and gaseous ammonia and consists in the use of ammonia in concentrations of approximately 150 to 300 grammes per cubic metre of chamber capacity and at temperatures of about 37 to 45° C. The hides are previously soaked or

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wetted according to condition and are hung in a chamber, steam being admitted to raise the temperature and maintain a degree of humidity. Ammonia is admitted at the same time in the concentrations indicated and after three to six hours when the roots of the hairs have been slackened the ammonia is expelled from the chamber and that remaining in the hides is dissolved by rinsing either in the form of ammonia or after conversion into a suitable salt, such as ammonium carbonate, by admission of carbon dioxide or flue gases. The hairs are removed by hand or mechanically, the hides being kept warm by immersion in warm water or otherwise until the depilation has been effected.

Tanning Leather. British Patent 175,329. T. B. CARMICHAEL, Waterloo, near Liverpool, and W. H. OCKLESTON, Bourn, Cambridgeshire. Oct. 1, 1920, No. 27,837. Hides and skins are subjected to a preliminary tanning by a mixture of formaldehyde and sodium bisulphite in solution, and are afterwards tanned by pyrogallol, catechol, or other tanning-agents, precipitation of which is prevented by the preliminary process.

Tanning. British Patent 175,362. T. B. CARMICHAEL, Waterloo, near Liverpool, and W. H. OCKLESTON, Kelsall, Cheshire. Nov. 8, 1920, No. 31,494. After mineral or vegetable tanning, hides are soaked in an aqueous solution of pyridine to fix the tanning-elements and permit subsequent washing and rapid drying without sweating or exudation to cause streaking or discoloration. The hides are usually soaked for four to twelve hours in a 10 to 25 per cent solution of pyridine. In the case of vegetable tanned hides, subsequent washing is effected in a 5 per cent solution of oxalic acid or in weak aqueous solutions of other organic or inorganic acids, such as formic or sulphuric acid. The application of the treatment to chrome and alum tanning processes is referred to.

Tanning. British Patent 175,620. SOC. DU FEUTRE, Paris Feb. 9, 1922 No. 3,872. Hides are soaked in slightly acidulated water before treatment with lime in the hair-removing process, so that the hair or wool, which retains a relatively large amount of the acidulated water by capillarity, is not attacked by the lime, which nevertheless easily traverses the skin after neutralizing the acid held therein. The soaked hides are piled in pairs with their skin sides together, each pair being separated by a waterproof fabric to protect the hair from the lime in the adjacent skin, and are treated in the usual manner with a somewhat larger amount of lime.

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1922

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ACTIVE

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Witherell, A. L., % Fred Rueping Leather Co., 96 Doty Street, Fond du Lac, Wisconsin.

Neeld, P. I., 826 65th Ave., Oak Lane Park, Philadelphia, Pa.

ASSOCIATE

Hatton, Julian B., % Eagle-Ottawa Leather Co., Grand Haven, Mich.

Schell, A. B., 211 North First Street, Olean, N. Y.

Umholtz, R. B., Buena-Vista, Rockbridge County, Va.

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CHANGES OF ADDRESS

Bateson, M., 21 Calder Avenue, Littleborough, nr. Manchester, England.
Eysenbach, G. G., 102 Woodside Ave., Narberth, Pa.
Lorenz, J. B., % Helburn Thompson Co., 16 Goodhue St., Salem, Mass.
Morrison, J. A. S., Red Garth, Chester Road, Grappenhall, nr. Warrington, England.
Ritter, H. S., % Vacuum Oil Co., Tanners' Dept., 61 Broadway, New York, N. Y.
Sheard, Lawrence, Tonge Moor, 147 Thicketford Rd., Bolten, England.
Wallin, E. A., 703 Washington St., Olean, N. Y.

NOTICE

A photograph of the A. L. C. A. group taken at Bigwin Inn may be had by sending your order accompanied by $1.00 to H. C. Reed, Secretary, 22 East 16th St., New York City.

THE NINETEENTH ANNUAL MEETING

The nineteenth Annual Meeting of the A. L. C. A. held at Bigwin Inn, Lake of Bays, Canada, June 21, 22 and 23 was a most successful and enjoyable occasion. Unique in the fact that it was the first time in the history of the Association that an annual meeting was held outside of the States, the Association was extremely fortunate in its choice of Bigwin Inn for such a meeting. The Inn which is a charming place in a charming location was entirely devoted to the comfort and pleasure of the members and their families. Much credit is due to the management of Bigwin Inn for their liberal hospitality and their success in making the occasion a very enjoyable one, indeed. Under such happy conditions the meeting proved to be a regular "get together" meeting.

The papers presented at the meeting covered a wide range of topics of general and specific interest to the leather chemists and tanners. The meeting was opened on Wednesday morning, June 21st, by the address of the President, F. H. Small, which is published in this issue. The report of the Secretary-Treasurer, H. C. Reed, followed. The report of the Secretary showed that the membership of the A. L. C. A. on June 1, 1922, was as follows:—

Active and associate members	417
Mutual members	83
Total membership	500

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The Treasurer's report was rendered for the five months, January 1st to May 31st, 1922, and in summary was as follows:

General Account

Income		$2,757.96	
Expense	$1,312.18		
Loans paid	1,179.00	2,491.18	
			$266.78

Journal Account

Income	$2,340.25	
Expense	2,101.01	
		$239.24
Net income		$ 506.02
Cash in bank Jan. 1st, 1922		2,295.22
Cash in bank May 31st, 1922		2,801.54
Assets	$6,443.05	
Liabilities	505.09	
Net worth	$5,937.96	

The program was as follows:—

Committee Report.—Determination of Moisture in Leather
F. P. Veitch.

Influence of Atmospheric Humidity on the Strength and Stretch of Leather.....F. P. Veitch, R. W. Frey and L. R. Leinbach.

Committee Report.—Determination of Epsom Salts in Leather
R. W. Frey.

Comparative Observations of the Tanning Properties of Vegetable Tanning Materials, Synthetic Tans and Mixtures of Vegetable Tanning Materials with Synthetic Tans
S. Kohn, J. Breedis and E. Crede.

Committee Report.—Synthetic Tanning Materials..T. A. Faust.

Committee Report.—Determination of the Astringency and Penetrating Value of Tan Liquors .....R. O. Phillips.

Wednesday Afternoon

Preservation Effects of Oils and Greases on Leather
F. P. Veitch, R. W. Frey and L. R. Leinbach.

Distribution of Grease in Leather.....L. Balderston.

Committee Report.—Determination of Oils and Greases in Leather .....W. K. Alsop.

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The Mode of Occurrence of Tannin in the Living Cell
F. E. Lloyd.
The Diseases of the Chestnut Tree.....E. Schell.
The Bacteriology of the Fresh Steer Hide
G. D. McLaughlin and G. E. Rockwell.
Bacteriology as a Fundamental Science and Its Relation to Tanning .....W. B. Wherry.

Thursday Morning

Some Observations on the History of Bating Skins
C. S. Hollander.
Committee Report.—Rapid Washing of Chromed Hide Powder .....F. F. Marshall.
A Possible Theory of Chrome Tanning
W. R. Atkin and F. C. Thompson.
Progress in the Physical Chemistry of Gelatin....C. R. Smith.
Committee Report.—The Determination of Water-Soluble in Leather .....G. W. Schultz.

Thursday Afternoon

Time Reduction in the Tanning Process.....R. O. Phillips.
A Layman in Research.....F. M. Moffat.
The Practice of Curing Heavy Hides
G. D. McLaughlin and E. R. Theis.
The Science of Hide Curing
G. D. McLaughlin and E. R. Theis.
Committee Report.—The Direct Measurement of the Plumping Power of Tan Liquors .....V. J. Mlejnek.
The Versatility of a Plumping Method.....H. C. Reed.
The Plumping of Hide Powder by Lactic and Acetic Acids
J. S. Rogers.
The Importance of Finish in the Cutting and Marketing of Sole Leather.....H. B. Smith.

Friday Morning

Committee Report.—Determination of Glucose in Leather
I. D. Clarke.
Committee Report.—Comparative Analysis of Tanning Materials.....H. C. Reed.
Modern Problems in Chrome Tanning.....D. Burton.

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Committee Report.—Chrome Leather Analysis..L. Balderston.
Committee Report.—Color Measurement of Vegetable Tanning Solutions.....T. Blackadder.
Treatment of Tannery Wastes.....E. B. Besselievre.
Committee Report.—An Alternative Filter Paper for Soluble Solids Filtration.....L. M. Whitmore.

Most of the committee reports have been published in preceding issues of this JOURNAL. Of the three papers from the Department of Leather Research of the Tanners' Council, that one on the Bacteriology of the Fresh Steer Hide was published in the July number; the two on the Science of Hide Curing and the Practice of Curing Heavy Hides appear in this number. The remaining papers will appear in subsequent issues.

Before the close of the open meeting, President Small announced the receipt of messages conveying hearty good wishes for a successful meeting from E. A. Brand, Secretary of the Tanners' Council, Prof. D. McCandlish, R. W. Griffith and D. Burton, Chief of the Leather Section, C. W. S. Research Department, Manchester, England. Mr. Brand re-affirmed his desire to aid the leather chemists at all times. This desire has been amply demonstrated in the past by the hearty assistance rendered the Association. It is worthy of note that the several messages received from members of the S. L. T. C. express the desire of a closer mutual co-operation in our common endeavors. The same expression was received from Dr. Gansser, President of the Association of Swiss Leather Trades' Chemists in behalf of his Association.

President Small mentioned several occasions in the past year when the A. L. C. A. was called on and rendered active assistance to the Tanners' Council, after which the meeting resolved into executive session.

The committee appointed to audit the books of the Association reported that they were found to be complete and accurate.

In recognition of the interest shown in the success of our meeting and the hospitality extended to us a motion was made, seconded, and passed by a unanimous rising vote that the Secretary be authorized to send a letter of thanks and appreciation to Mr. Shaw and Mr. Mosbaugh.

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The tellers of the ballot reported the election of C. C. Smoot, 3rd, President, J. S. Rogers, Vice President, C. R. Oberfell and R. W. Griffith, ordinary members of Council.

At the conclusion of the meeting a hearty rising vote of thanks was given to the retiring President on the motion of G. D. McLaughlin, in recognition of the inestimable service rendered in successfully conducting the affairs of our Association through the most critical period in its history.

PRESIDENTIAL ADDRESS *

By F. H. Small

This Nineteenth Annual Convention of The American Leather Chemists Association which we now are opening is unique in that for the first time since the inception of the Association we are meeting outside our home country. While for many years our Association has been cosmopolitan in its membership, this is the first occasion when we have enjoyed the hospitality of any of our non-resident members. May we not accept the event as an augury of a community of interest that recognizes no bounds of country? If in specific details the problems of our industry vary from country to country, the science of the industry, which is the particular phase that our Association is trying to advance, is universal, and in heartiest good fellowship we all may unite in helping to make tanning a science and not an art. Much progress comes from friendly and frank discussion, and it is altogether possible that this incursion of ours into a neighboring country may, because of the different point of observation entailed, throw new light on some of our own home problems.

Is it not even worth considering whether the attrition of broadly varying modes of thought which should ensue from a joint meeting of our Association and the Society of Leather Trades Chemists might not be productive of enlightenment so beneficial as to warrant strenuous endeavor to bring about such meeting even though distance makes accomplishment difficult? Whether or not we may have such joint meeting to look forward to, we are pleased at this time to be here with our Canadian friends.

* To the Nineteenth Annual Meeting at Bigwin Inn, Lake of Bays, Canada, June 21, 1922.

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As to our Association, I am greatly delighted to be able to report its condition eminently sound and healthy. Numerically, we do not measure up to our size of a year ago, due to a loss of sixteen in our Mutual Membership, but we show a net gain of five in our Active Membership and a net gain of 5 in our Associate Membership, giving us a present total membership of an even five hundred. In the phraseology of the day, "that's good work, but 'taint enough." The past year has not been a favorable one for a membership campaign because of trade conditions, but a better industrial situation should warrant such campaign and we should not rest content until all the tanners as well as chemists are enrolled in our Association.

Financially, we once more may hold up our heads and throw out our chests. We have paid back all borrowed money, we have redeemed our Liberty Bond, and unless our calculations are awry, we should arrive at the first of January next with a cash balance of nearly $2,000, exclusive of our Liberty Bond holding and of a reserve fund of approximately $1,000, set up for reprints of back numbers of our JOURNAL. Again we may say to those responsible, "good work." We are living within our income. The growing circulation of our Journal should enhance materially its value as an advertising medium and assure us of a larger revenue from this source. We should be able to increase our Associate Membership largely and thus also add to our revenue. A respectable reserve against unknown increased expenses such as have faced us in recent years should be set up and provision made for the enlarged activities of the Association which necessarily accompany its endeavors to make itself of the most value to the industry, after which I believe serious consideration should be given to the possibility of lessening the annual dues.

Studiously, there are several outstanding items in our work of the year. First, it seems to me that a start has been made towards some understanding of the synthetic tanning materials. Greater knowledge of them is necessary before any tanner can use them with comfort. He should be able to assure himself that successive shipments are uniform; should be able to measure

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the active and valuable ingredients and to determine what and what percentage of inert or positively harmful ingredients are present. Until he can secure knowledge of this sort, these materials must fail of achieving that sphere of usefulness to which they legitimately may be entitled.

Again, a start has been made toward the better understanding of leather composition as shown through analytical dissection. For a long time we have inserted in our reports an arbitrary, purely empirical figure which we have been pleased to call the "water-soluble" percentage. In recent years an attempt to give this a scientific meaning has been made through carrying the extraction of the water-soluble to an ultimate, but this failed through inability to reach a definite end, and through evident breaking down of the leather compound during the process of extraction. This year the problem has been attacked from a different angle and an endeavor made to give the figure meaning as a measure of material in the leather in no way fixed. The problem is a difficult one, but as any real understanding of leather composition is bound up in it, it merits our most exhaustive study.

Further work has been done on the method proposed by Mr. Claflin for measuring the plumping action of solutions on hide. The method cannot yet be recorded as more than approaching final form, but even in its present condition, it possesses possibilities of information deserving of most respectful consideration. Acid values of liquors for long have been known to be erroneous measures of plumping value; hydrogen ion concentration, according to Atkin, (*Journal of S. L. T. C.*, Volume 6, No. 4, Page 138) fails to show the effect of all influencing factors and does not tell a wholly accurate story of plumping value. In the Claflin method, every factor influencing plumping plays its part and the measure obtained is the resultant of all these factors. While the method needs further study, and unfortunately is in its nature empirical, it probably gives a maximum of information concerning plumping value for a minimum expenditure of time and money, and it would seem worthy of serious consideration whether in the near future our present method for the determination of the acidity of tan liquors should not be substituted by a method for the determination of plumping value.

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This Convention is likely to prove notable, even epoch-making, in that it will receive the results of the work done by the Research Laboratory of the Tanners' Council on the Science and Practice of Curing Heavy Hides. This report, to the best of my knowledge, embodies a record of the most elaborate and authoritative work ever done on the subject, and should be of great value to the tanner in enabling him to understand the reason for various vagaries of hide behavior in his tanning processes,—but more important still, should make possible a rational and intelligent procedure for preserving hide in the best condition for the tanner's use.

Please notice that these various matters which I am bringing to your attention are of direct and immediate concern to the practical tanner. They affect his practice of leather making and bear on the economy of production and the quality of his product. I wish to stress this point, because I believe a large measure of the usefulness of our Association lies in the assistance which it can bring to the leather makers of the industry.

To bring about an increased knowledge on the part of the tanners of the work of our Association, to develop a sympathetic understanding of our efforts and aims, to secure such measure of co-operation between our Association and the Tanners' Council as common interests may warrant, has been one of my special desires during my term of office. While I have failed of full accomplishment, I feel hopeful that progress has been made. Much of the work we are doing is intensely practical—there is no man making leather to-day who should not be able to better his manufacturing operations and the quality of his product through the information contained in the pages of our JOURNAL. Some way should be found of bringing this home to the tanner, of illustrating to him the urgency of his need of this information so that he will know that he cannot do without it. Each and every one ought to be enrolled in our list of members.

The original aim of our Association was a method of tanning analysis. We rapidly outgrew this and each year saw our aims and activities broaden. The possibilities for usefulness are unlimited. May we continue to grow up to them.

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SCIENCE OF HIDE CURING *

By George D. McLaughlin and Edwin R. Theis
FROM THE DEPARTMENT OF LEATHER RESEARCH, OF THE TANNERS' COUNCIL, IN THE UNIVERSITY OF CINCINNATI

When an animal is slaughtered the interest of both tanner and leather chemist begins. This has been largely unrecognized, yet, as we have shown,[1] the kind of treatment a hide receives in the hide-cellar largely determines its future value. When undesirable, irreversible changes occur in a hide during curing, usually no amount of skill in tanning will off-set them. The science of curing is the first step in the science of tanning. Tanning literature contains many generalizing statements regarding curing, but we are unable to find any systematic study, based on experimental evidence. The practical methods of curing and the application of the facts herein given are detailed in the article which accompanies this one.[1]

Study of curing divides itself into two interdependent phases; colloid-chemical and bacteriological. This article deals with the first, the second will be discussed elsewhere.[2] What could be more stimulating to the thinker in the colloid-chemical, physiological and bacteriological phases of tanning science than the whole problem of curing? Let us proceed with its discussion.

1. Morphology. The hide is made up of four general layers; —the hair; the epidermis; the corium or true skin; and the adipose tissue (flesh and fatty material). The weight proportion of each layer (eliminating the hair) and the original water content of each is shown in Table I.

TABLE I.—SUMMER STEER, SAMPLES FROM ALONG BACK BONE, 12 INCHES FROM ROOT OF TAIL

	Epidermis	Corium	Adipose tissue
Per cent weight of total	20.40	49.82	29.78
Per cent water content	74.35	61.00	54.10

In other words, 100 grams of blood weight hide contain 61.66 grams of water, 25 per cent of which is in the epidermis, 49 per cent in the corium and 26 per cent in the adipose tissue.

* Read at the Nineteenth Annual Meeting of the A. L. C. A., Bigwin Inn, Ontario, Canada, June 22, 1922.

[1] See accompanying article, Practice of Heavy Hide Curing.

[2] In preparation.

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2. *Curing,* considered from a physical viewpoint, is a movement of salt into the hide, and water out. A parallelism exists between the two phenomena.

If fresh hide is covered on both sides with C. P. NaCl crystals and allowed to stand for varying periods of time, we find on chemical analysis of the hide, at the end of the selected periods of time, a definitely paralleled dehydration and salt absorption. If fresh hide is placed in a 25 per cent NaCl brine for varying periods of time, we again note the parallelism between dehydration and salt absorption. Experimental data is given in Table II and Figure 1.

In practice a cured hide which has been brined may show a somewhat greater shrinkage from blood to cured weight than if not brined. In Table II and Figure 1, we note that salting produces a greater shrinkage at the end of 24 hours than brining. If the brined hide is treated at the end of the 24-hour brining period with dry salt (as in practice) a sharp increase in shrinkage is noted.

The salt absorption figures of Table II apply to either one hide or to many hides piled on top of each other; except, in the latter case, the hides at the bottom and top of the pile absorb slightly more salt than those in the middle. In specific figures for the various layers of the pile, the bottom hides contain 11 per cent more salt and the top hides 6 per cent more salt than the middle layers, at the end of 24 hours' salting.

Examination of Table II and Figure 1 shows the movement of salt and water in opposite directions, the salt moving into the hide, the water out. Dehydration is effected only when the salt moves into the hide; it is not a mere surface action.

3. When fresh hide is salted on both sides, for varying periods of time, and its various layers (epidermis, corium and adipose tissue) are then analyzed for water and salt, the results shown in Table III and Figure 2 are obtained.

The original hide (minus hair) contained 61.66 per cent of water; while at the end of 24 hours of salting, it contained 40.78 per cent; in other words, 100 grams of original hide had lost 35.23 grams of water. Of the total water lost in 24 hours, 25 per cent was lost by the epidermis, 41 per cent by the corium and 34 per cent by the adipose tissue. Of the 5.90 grams of salt

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TABLE II.—DEHYDRATION AND NaCl ABSORPTION

Salting					Brining in 25% NaCl Solution			
Hrs. treatment	% Shrinkage	% Dehydration	% NaCl absorbed	Ratio: Dehydration / Salt absorbed	% Shrinkage	% Dehydration	% NaCl absorbed	Ratio: Dehydration / Salt absorbed
1	−5.37	−6.91	+1.54	4.49	−5.76	−8.15	+ 2.39	3.41
2					−8.96	−11.62	+ 2.66	4.37
3	−10.45	−13.81	+3 36	4.11	−9.63	−13.12	+ 3.49	3.76
4	−12.79	−16.68	+3.89	4.29	−10.90	−15.06	+ 4.16	3.62
5	−16.45	−20.76	+4.31	4.81	−11.81	−16.48	+ 4.67	3.53
24	−23.85	−30.51	+6.66	4.58	−13.45	−21.21	+ 7.76	2.74
					(Regular salting began)			
					Hrs.			
					27	−19.45		
					48	−23.65		
					72	−29.20		
				Av. = 4.46				Av. = 3.57

The parallelism between dehydration and salt absorption is more evident when the ratio Dehydration : Salt absorption is considered, being in the case of brining 3.57 and in the case of salting 4.46.

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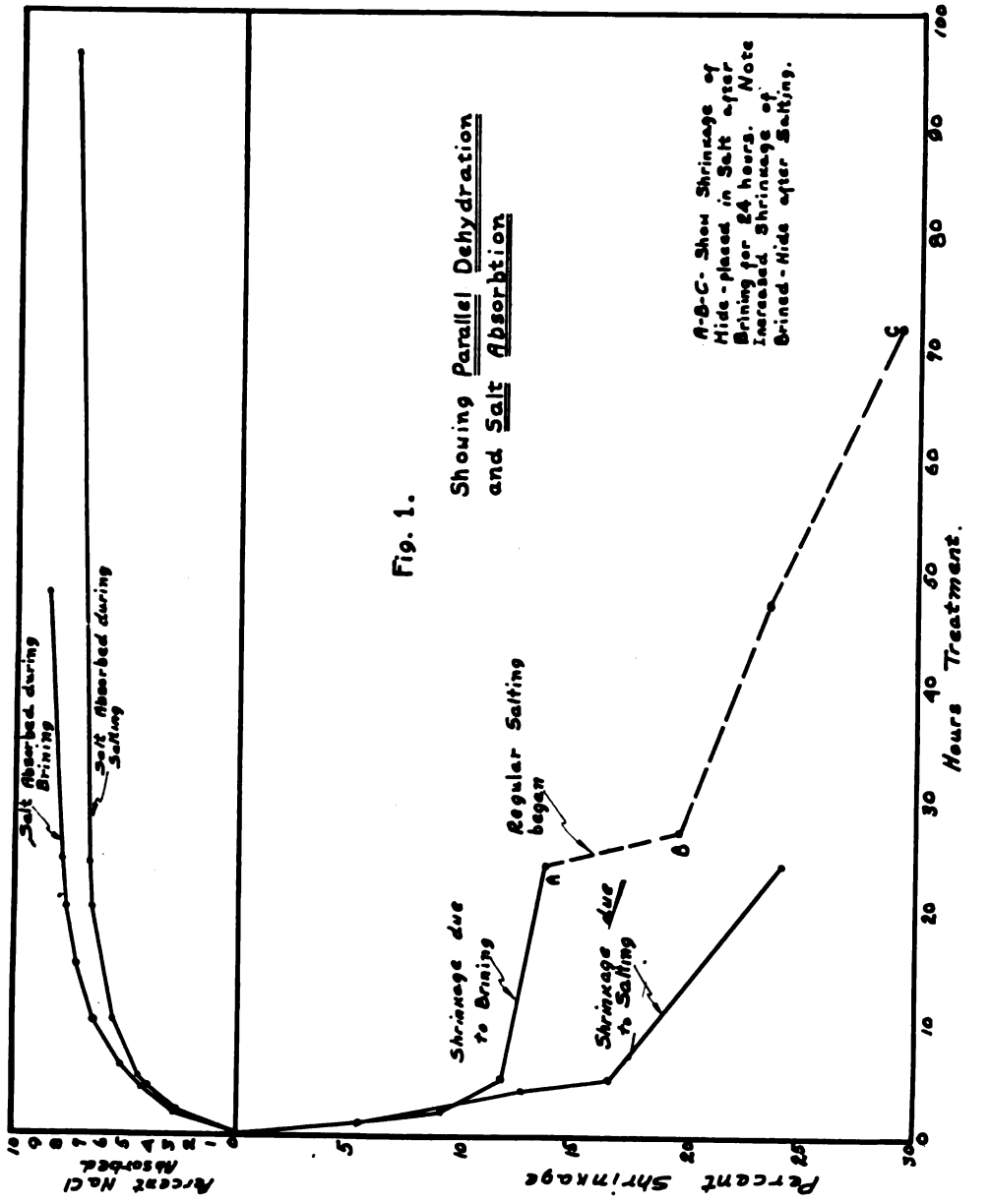

Fig. 1.

Showing Parallel Dehydration and Salt Absorbtion

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TABLE III.

	Epidermis		Corium		Adipose tissue		Total % NaCl of whole hide	Total % H_2O of whole hide
	H_2O	% NaCl	H_2O	% NaCl	H_2O	% NaCl		
Control	74.35		61.00		54.10			61.66
1 hr. salting	74.00	0.423	57.25	0.798	50.00	0.282	1.503	60.41
4½ hrs. salting	71.75	0.846	52.85	2.090	46.60	0.372	3.308	57.07
24 hrs. salting	54.75	1.096	45.30	3.780	22.30	1.026	5.902	40.78

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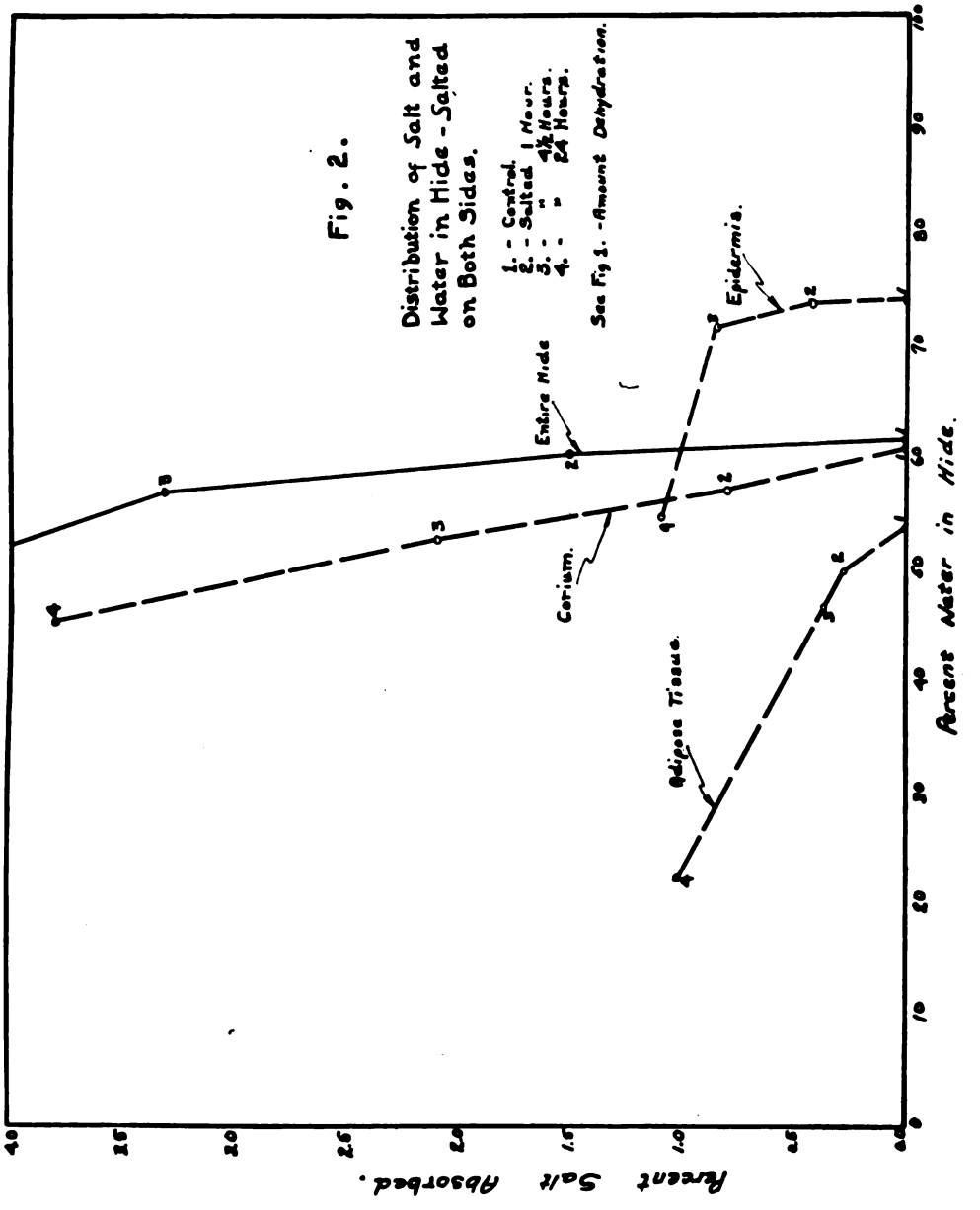

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absorbed, the epidermis took up 1.12 grams (19 per cent); the corium 3.78 grams (64 per cent) and the adipose tissue 1 gram (17 per cent); or for each gram of water lost by the epidermis it took up 0.124 gram NaCl, the corium 0.264 gram and the adipose tissue 0.085 gram. The ratio $\frac{\text{dehydration}}{\text{salt absorption}}$ was greatest in the adipose tissue and least in the corium. When fresh hide is brined 24 hours in 25 per cent salt solution, the proportionate salt distribution throughout the hide layers is so relatively identical to the distribution in the case of salting that it is unnecessary to detail the results.

4. The rate of salt diffusion through the epidermis on the one hand and through the adipose tissue on the other is different. What is the result when hide is salted on hair side only; on flesh side only; or on both sides? The amount of salt absorbed in 24 hours when hair side alone is salted, is only one twenty-fifth as much as is absorbed when the hide is salted on the flesh side alone, or on both sides. The epidermis is primarily an organ of secretion and not of absorption. When salted on hair side only, for so long a period as 24 hours, however, the salt will have diffused through the epidermis and the corium and reached the adipose tissue. Table IV shows these facts.

We note from Table IV that the salt absorption when hide is salted on both sides is no greater than when salted on the flesh side only. The salt absorption is necessarily directly governed by the amount of water present for its solution. The only water present is that contained by the hide and blood. When salt is placed on the flesh side alone, dehydration occurs in one direction only, but when salt is placed on both sides, dehydration occurs in two directions. There is a definite quantity of "bound" water in the hide (approximately 62 per cent). When dry salt is placed on the flesh side, the surface moisture dissolves part of the salt, forming a nearly saturated brine, which diffuses into the interior of the hide, extracting water as it goes; as water is extracted, more salt is dissolved, until a physical equilibrium is obtained, at which point dehydration and salt absorption cease. When salt is placed on both sides, the total quantity of "bound" water, available for brine formation, remains the same, even

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TABLE IV.

	Total % NaCl absorbed	% Of total NaCl absorption in epidermis	% Of total NaCl absorption in corium	% Of total NaCl absorption in adipose tissue
Salting hair side only, 1 hr.	None	None	None	None
Salting hair side only, 4½ hrs.	None	None	None	None
Salting hair side only, 24 hrs.	0.2273	23	59	18
Salting flesh side only, 1 hr.	1.2045	28	62	10
Salting flesh side only, 4½ hrs.	2.9730	23	66	11
Salting flesh side only, 24 hrs.	5.7025	18	67	15
Salting both sides, 1 hr.	1.0525	28	53	19
Salting both sides, 4½ hrs.	2.8570	26	53	11
Salting both sides. 24 hrs.	5.4525	19	64	17

N. B. All calculations in Table IV are based on the weight of the fresh hide, with the weight of the hair excluded.

though the amount of salted surface is doubled. In addition we have seen that salt is absorbed through the epidermis very slowly.

In the foregoing, we have mentioned a nearly saturated brine formed by salt and the "bound" water of the hide. What is the nature of this hide brine? When salt is dissolved in water, we have a simple homogeneous system, but when "hide brine" is formed on the surface of the hide, we have a much more complex system, namely, NaCl—Water—Blood. The blood present retards the absorption of salt by the hide; these effects will be described later.[3]

We collected samples from pools of brine which had run off of cured hide packs in four different cellars. Their composition is shown in Table V.

TABLE V.—Showing Blood Content of Packing House Brines

	% NaCl*	% Blood*
Hide cellar No. 1	29.85	7.94
Hide cellar No 2	29.40	14.21[1]
Hide cellar No. 3	29.80	8.75
Hide cellar No. 4	29.60	7.44

*These percentages are based on volume.

[1] Pack not closed.

[3] The drastic effect of this dissolved blood upon the antiseptic power of brine, will be dealt with in another publication.

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5. In Sections 2 and 3 we have dealt with immediate salting or brining only, (within 30 minutes after killing). What is the effect of delayed salting or brining upon the salt absorption and dehydration? This, to our minds, is the *Crux of the Problem of Curing.*

If salting is delayed from one to six hours after killing, the rate of diffusion of salt into the hide, is always greatly reduced in consequence of the delay. If hide is allowed to stand for varying periods of time between killing and salting, the rate of salt absorption is different for each period of delay, decreasing approximately as a simple exponential function. This is true whether the hide is exposed to atmospheric conditions or not, proving that surface evaporation is not, under normal conditions, the determining factor.

Similar experiments, immersing hide in 25 per cent brine, showed analogous results, excepting that the rate of absorption of the brined hide was always greater than the corresponding salted hide, as can be seen by comparing Tables VI and VII and Figure 3.

Table VIII shows similar data covering longer periods of salting or brining treatment.

TABLE VI.—Showing Ability of Hide to Absorb Salt after Varying Perids of Delay in Salting;—Salted for One Hour

	After delay of				
Per cent NaCl in	immediately	1 hour	2 hours	4½ hours	6 hours
Adipose tissue	0.178	0.237	0.174	0.067	0.062
Corium	1.020	0.601	0.518	0.183	0.210
Epidermis	0.457	0.303	0.344	0.137	0.154
Total	1.655	1.141	1.036	0.387	0.425
Comparative Absorption of NaCl	100	69	62.55	23.35	25.65

TABLE VII.—Showing Ability of Hide to Absorb Salt after Varying Periods of Delay in Brining;—Brined for One Hour in 25 Per Cent NaCl

	% NaCl absorbed	Comparative absorption of NaCl
Immediately	2.642	100
After 1 hr.	1.959	74.25
After 2 hrs.	1.787	67.75
After 6 hrs.	1.187	45.10

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Fig. 3.

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TABLE VIII.

When treated	Kind of treatment: Salted 1 hr.	Salted 4½ hrs.	Salted 8 hrs.	Salted 24 hrs.	Brined 1 hr.	Brined 4½ hrs.	Brined 8 hrs.	Brined 24 hrs
Immediately	1.726	3.746		6.510	2.642	3.372		6.324–7.761
After 1 hr.	1.214	3.225		5.520	1.959	4.462		6.720–7.380
After 2 hrs.	1.062	2.860		6.970	1.787	4.040		6.764
After 4½ hrs.	0.558			6.510				
After 6 hrs.	0.425			6.290	1.187			
After 18 hrs.			3.345				3.850	

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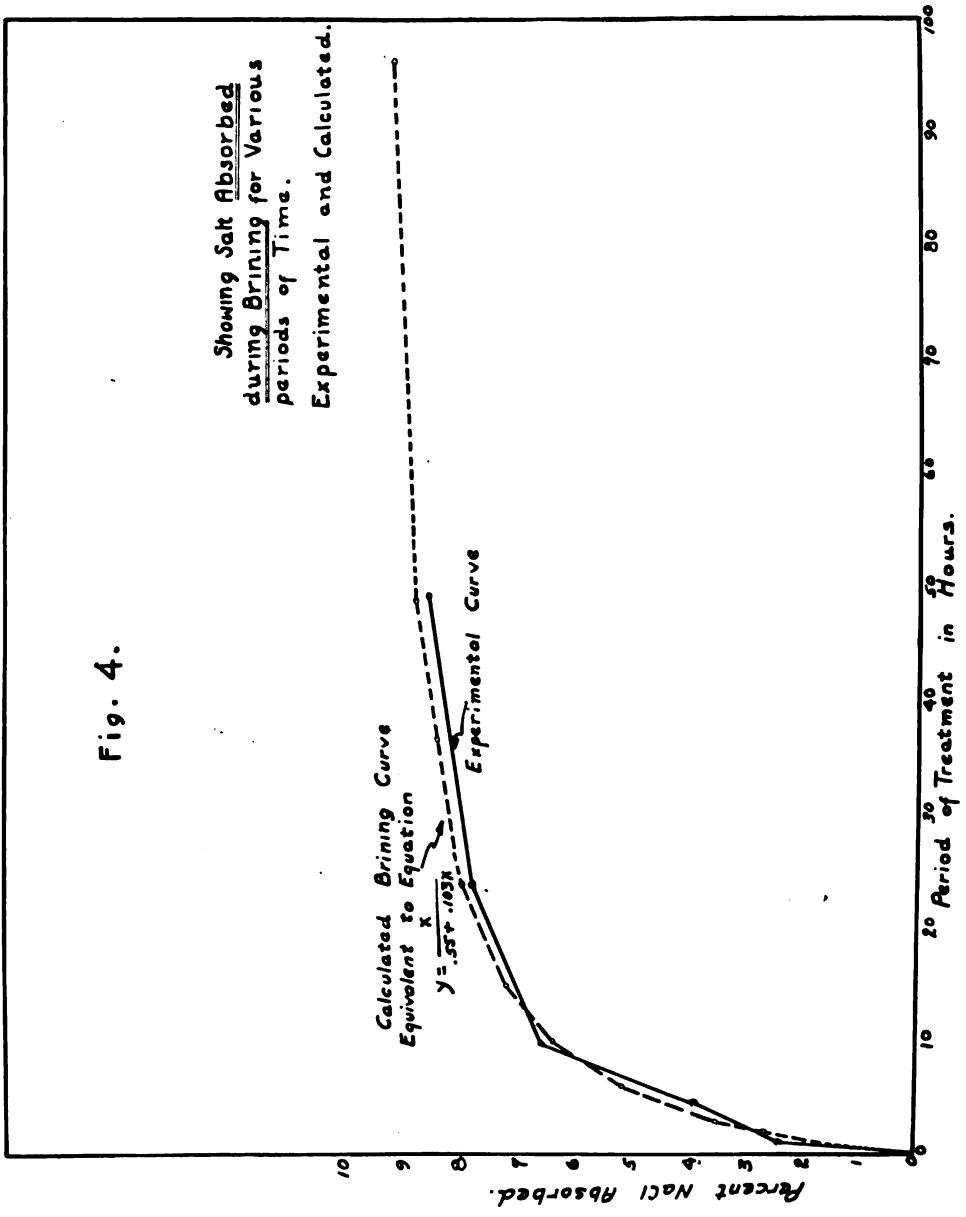

Fig. 4.

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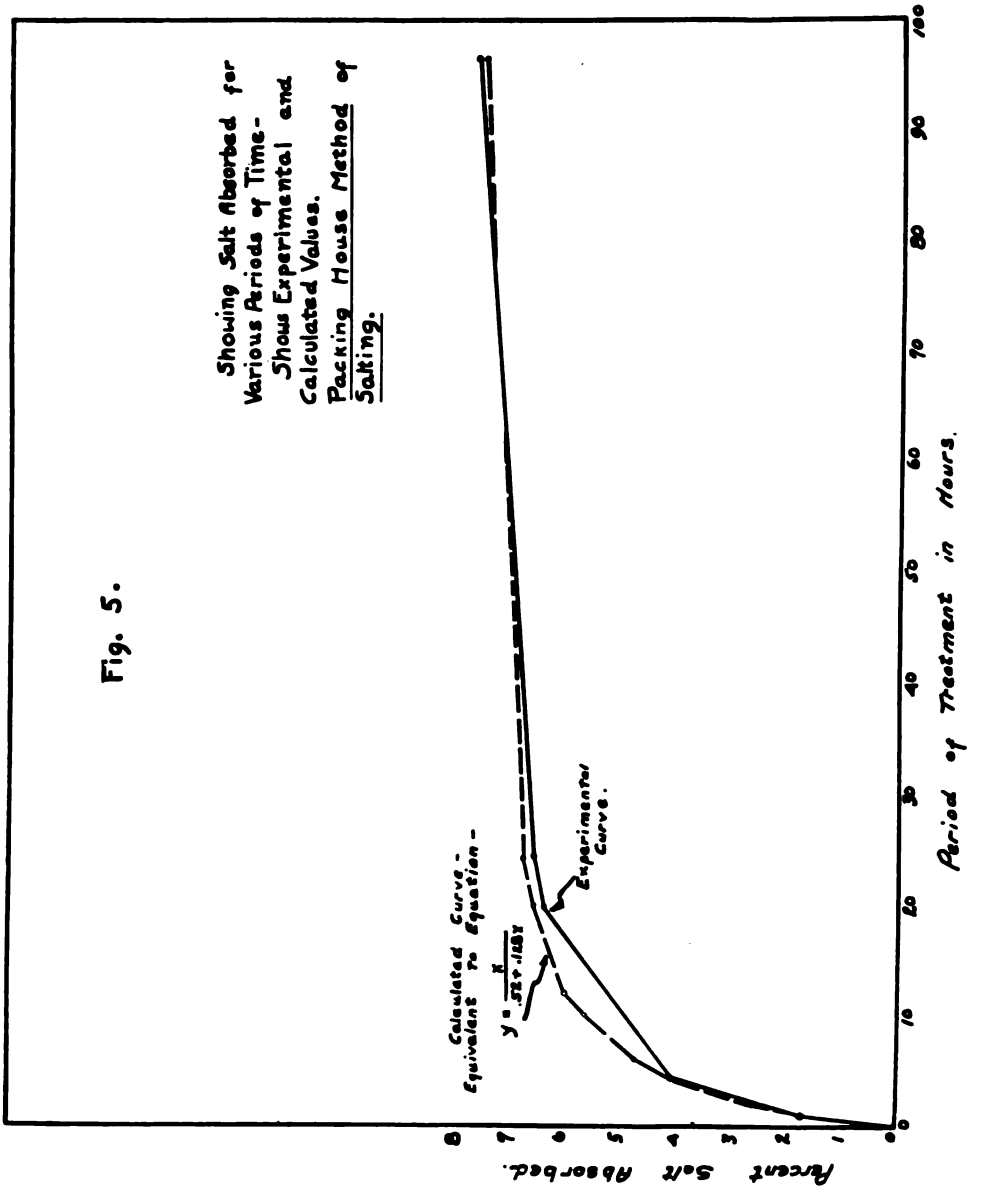
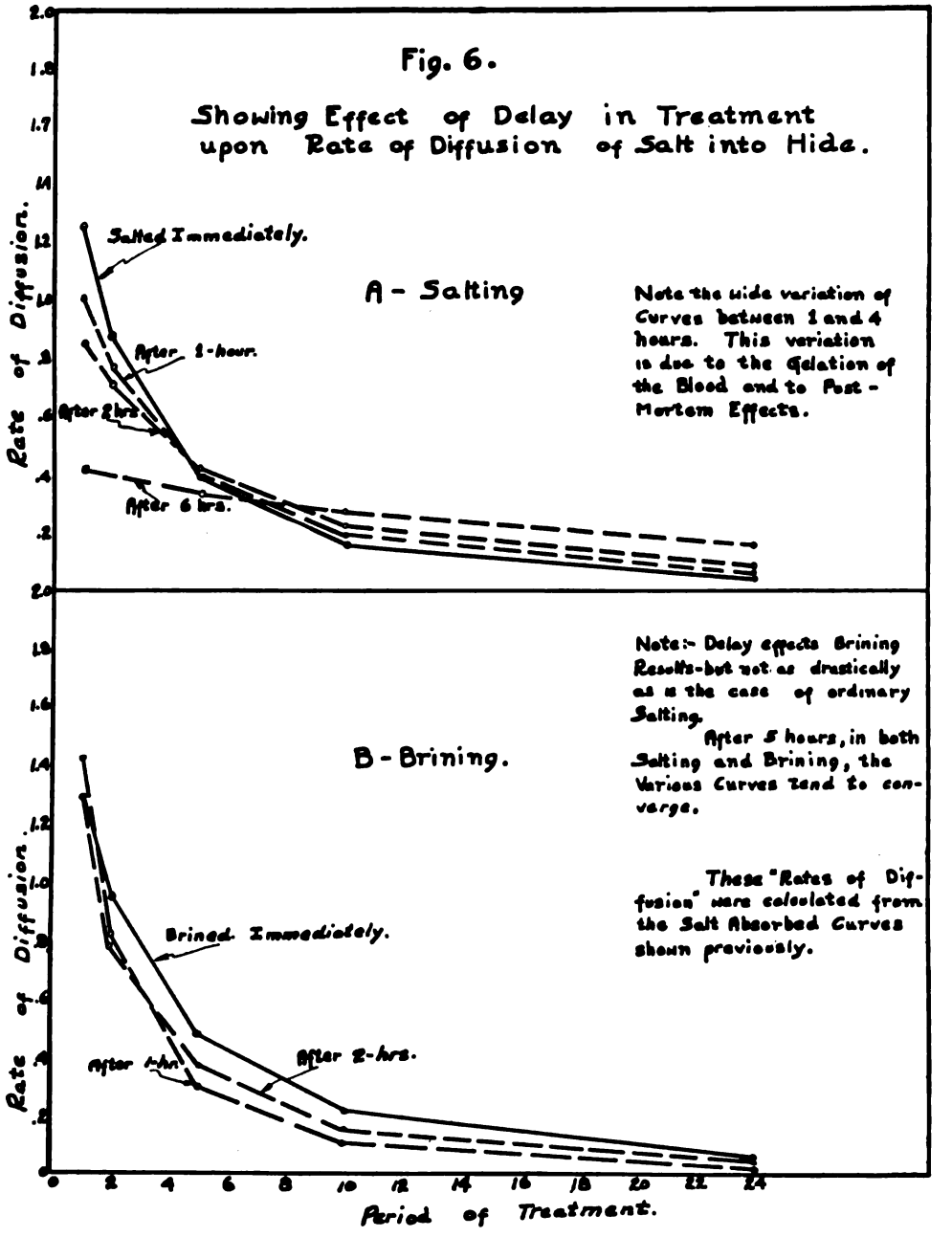

Showing Salt Absorbed for Various Periods of Time- Shows Experimental and Calculated Values. Packing House Method of Salting.
Calculated Curve- Equivalent to Equation -
Experimental Curve.
Percent Salt Absorbed.
Period of Treatment in Hours.

Fig. 5.



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6. We can now explain why delayed salting or brining results in a lessened rate of salt absorption, especially during the first few hours of treatment. Experimental data, in Tables VI, VII and VIII shows that in all cases of delayed curing treatment, the rate of salt absorption by the hide, for short periods of treatment, is always lower than that for hide salted or brined immediately. On the other hand, the salt absorption rate during the later hours of treatment shows higher. This demonstrates that hide that has been treated immediately, or treated after standing, all other conditions being equal, attains practically the same ultimate salt content. Figures 4, 5 and 6 show these phenomena. Figures 4 and 5 show actual salting and brining curves, in which the fresh hide was treated immediately. These figures also show calculated curves which apparently fit the general equation $y = \frac{x}{a + bx}$, where y = salt absorption, x = the hours of treatment and a and b empirically calculated constants. Figure 6 shows the decreased ratio of diffusion in the early hours of curing, resulting from delayed treatment. These rates were calculated by differentiating the general equation and applying it to the various curves. The diffusion rates are given in Table IX.

TABLE IX.—RATES OF DIFFUSION

Hours salting	Treatment: Immediate salting	Immediate brining	After 1 hour salting	After 1 hour brining	After 2 hours salting	After 2 hours brining	After 6 hours salting
1	1.235	1.301	1.000	1.431	0.852	1.291	0.409
2	0.861	0.954	0.764	0.818	0.692	0.776	0.398
5	0.386	0.480	0.402	0.298	0.416	0.376	0.334
10	0.161	0.221	0.188	0.107	0.219	0.152	0.267
24	0.041	0.063	0.053	0.023	0.072	0.037	0.158

These rates of diffusion were calculated from equations derived from experimental data.

Hide receiving either immediate or delayed treatment attains practically the same ultimate salt content. We are not specifically interested in the ultimate salt content, since this, in any given case, is more or less automatic. We have found this to be the case through analysis of hides in packs, as well as in laboratory experiments, where the results and curves are almost identical. We are vitally interested in the salt absorption rate

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during the first few hours of treatment, because the greater the salt absorption during the first few hours, the quicker the curing action.

Fresh hide which has been brined for one hour does not show signs of decomposition nearly as quickly as hide salted for one hour. A piece of hide salted one hour begins to decay or putrefy in 24-48 hours at 90° F., while for hide brined one hour, the period is twice as long at 90° F. Hide which has been salted on the hair side only, decays quickly, and the hair "slips," (even though the corium is intact), just as in the old "Sweating" process. That this decomposition is not due to blood is proven by the fact that the epidermis surface is generally free from adhering blood. These facts may possibly explain why hides which are improperly cured may show hair-slips while the corium is still in fairly good condition.

Does the surface blood, which covers the flesh side of hide after killing play a rôle in curing? If we take fresh hide and divide it into two parts, allowing the blood to remain on one piece, and removing the blood from the second, and then salt both in the regular way for varying periods of time (up to a certain point of equilibrium), we find on analysis of the two pieces of treated hide, that there is always a difference in their respective salt content. The hide which contained the blood layer shows a lower salt content than the hide which did not. This difference is shown in Table X, and graphically in Figure 7.

TABLE X.—IMMEDIATE SALTING: SHOWING EFFECT OF BLOOD UPON THE DIFFUSION OF SALT INTO HIDE

Length of treatment (salting)	Per cent NaCl absorbed		Per cent increased absorption
	with blood	blood removed	
1 hour	1.049	1.820	73
4½ hours	2.210	2.790	26
24 hours	6.360	6.510	2

If we allow the hide to stand for varying periods of time before salting, and then salt, all other conditions being the same, we find that the salt content of the hide containing the blood is again lower than the hide from which the blood was removed. We also find that the salt content of both hides is lower than in the first case (see Table X). Results as obtained, are tabulated in Table XI.

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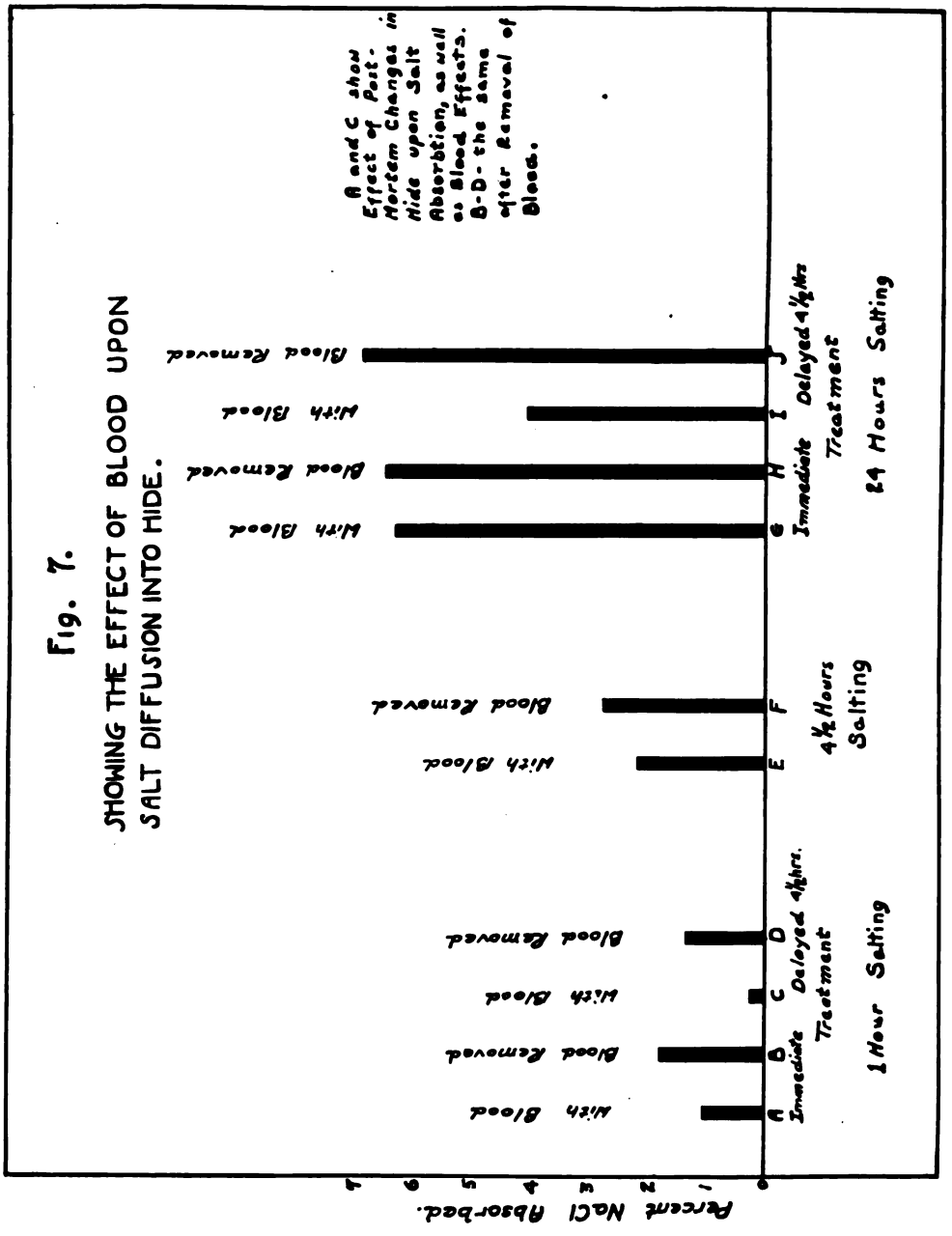

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TABLE XI.—DELAYED SALTING: SHOWING THE EFFECT OF BLOOD UPON THE DIFFUSION OF SALT INTO HIDE

Hours delayed	Length of treatment (salting)	Per cent NaCl absorbed with blood	Per cent NaCl absorbed blood removed	Per cent increased absorption
4½ hrs.	1 hr.	0.261	1.344	415
4½ hrs.	24 hrs.	4.110	6.920	68

The effect of blood, while very great, is not the only salt absorption retardant in the case of delayed treatment; otherwise the absorption of salt should be the same for immediate and delayed treatment, when blood has been removed. The almost equally important effect of post-mortem changes will be discussed in detail later.

Since blood has such a drastic effect, it is necessary to study further its retardation of salt diffusion. A thin blood membrane was made by immersing a small paper fat extraction thimble in fresh uncoagulated steer blood, pouring away the excess blood and allowing the thimble to drain. In this way a blood membrane was formed. A number of such tubes were prepared simultaneously. These tubes were allowed to stand for varying periods before the relative rates of salt diffusion were determined. The rates of diffusion were determined as follows: The tubes were first suspended in a beaker containing 100 cc. distilled water; 25 cc. of 25 per cent NaCl solution were placed in the tube. The salt was allowed to diffuse out through the blood film, into the distilled water. The amount of salt which diffused out in a given time period was determined and the results are shown in Table XII and Figure 8.

TABLE XII.—SHOWING RELATIVE RATES OF DIFFUSION OF SALT THROUGH BLOOD MEMBRANE (25 PER CENT NaCl SOLUTION)

Treatment	Ratio of diffusion
Immediate	100
½ hour's standing	100
1 hour's standing	75
2 hours' standing	74
3 hours' standing	42.5
4 hours' standing	39.7
24 hours' standing	85

Examination of both Table XII and Figure 8 shows that for the first few hours of the tube standing before diffusion, there is a rapid fall in the diffusion rate; but after the fourth hour the curve

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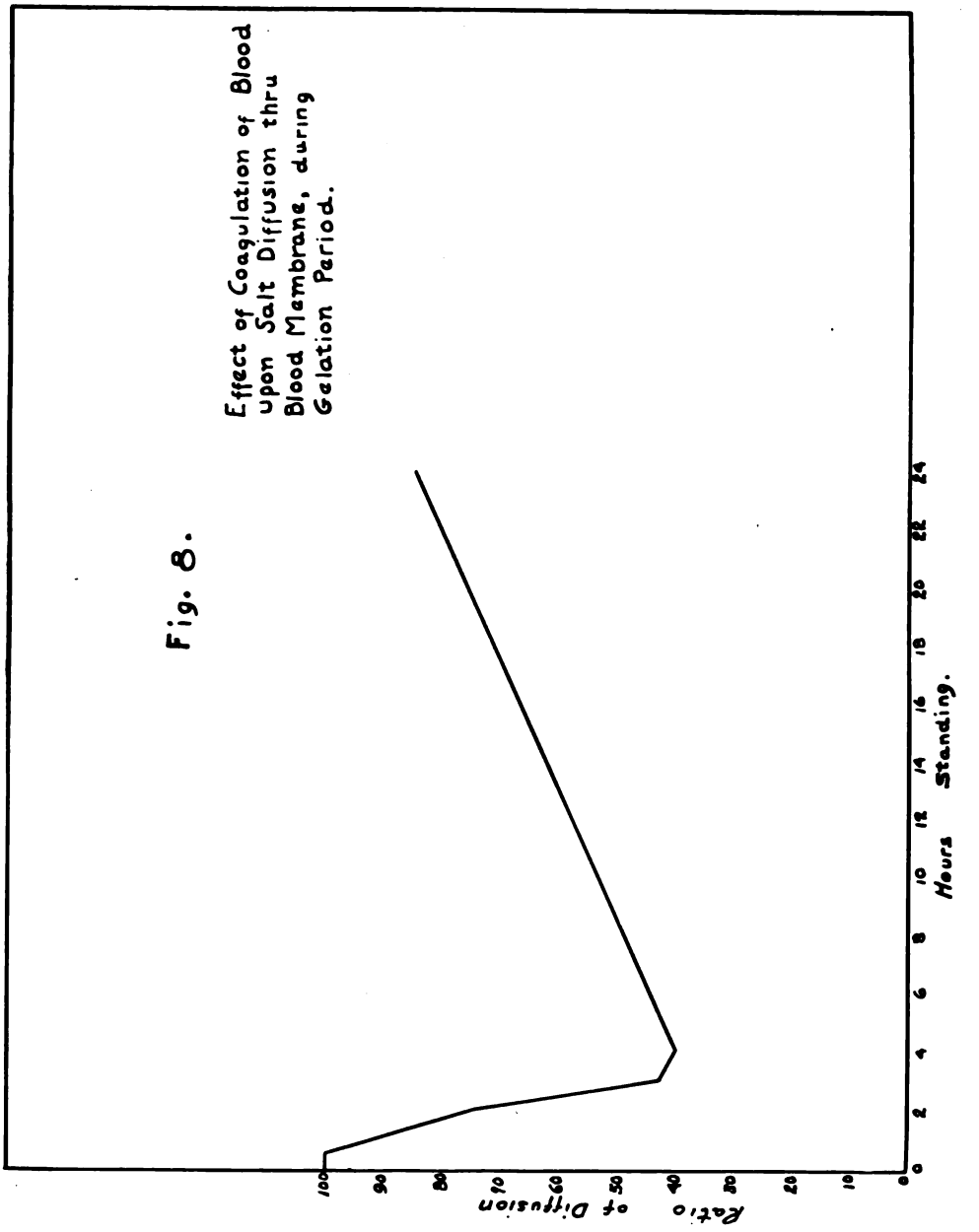

Fig. 8.

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rises, but does not attain the original relative 100, rising only to 85. In these experiments the temperature and humidity conditions of the hide cellar were maintained; however, even if tubes are kept in a warm room, the relative ratio does not change greatly.

Shortly after blood is shed it coagulates. It passes through a gelation period, which may be observed both microscopically and macroscopically. It is during this gel state of the blood that the salt diffusion is hindered. The gel begins to noticeably hinder diffusion (when at 51° F.) within about one hour from the animal's death. See Tables VI, VII and VIII. The gel may be slowly dehydrated and absorbed by the salt brine, or it will (if allowed to stand, untreated, long enough), dry out and crack, when in both cases its power of hindering diffusion diminishes.

7. If fresh hide is immersed for two hours in a 25 per cent salt brine containing 20 per cent of fresh blood; and if this brine is kept at various temperatures, analysis of the hide yields the results as tabulated in Table XIII.

TABLE XIII.

Temperature (F.)	25 Per cent NaCl: Control. No blood A	25 Per cent NaCl: 20 Per cent blood B	Ratio A/B
51° (Hide cellar temp.)	2.24 % NaCl	1.89 % NaCl	84.4
75° (Room temp.)	3.65 % NaCl	3.07 % NaCl	84.2
98.5° (Body heat)	3.43 % NaCl	2.47 % NaCl	72

The effect of blood present in a brine is very pronounced. We have mentioned previously that the brine running off the salted packs contains a high percentage of blood. Does the concentration of blood vary with the length of salting; or in other words, does the per cent of blood in hide brine vary from the first hours of their treatment until the pack is bundled?

TABLE XIV.—Showing Concentration of Blood in Salt Brine During Progressive Stages of Salting

	% Blood	Ratio
1st hour	42.6	100
3rd hour	21.4	50.2
4th hour	17.7	41.5
5th hour	14.2	33.3
24th hour	9.7	22.8
4 weeks	8	18.8

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In order to determine this point, the blood content in the brine formed during varying periods of salting was determined. The results are given in Table XIV.

8. One of us has shown that when an animal dies, certain post-mortem changes occur in its skin.[4] Do these post-mortem changes retard the absorption of salt by the hide? Table VIII shows that when hide is allowed to stand before treatment, there is a lessened salt absorption. Is this due solely to the blood jelly? Hide was washed free of blood and part salted immediately, while another part was allowed to stand for 4½ hours before treatment, and then salted. It was found that the hide (free from blood, in both cases) which had stood for 4½ hours without treatment, showed a lower salt content than did that which had been salted immediately.

Table XV and Figure 9 demonstrate a definitely lessened salt absorption when hide is allowed to stand before treatment; that the effect of blood alone is not responsible for this lessened absorption; that the effect of blood and post-mortem changes combined is very large.

9. The results obtained thus far are based upon the use of C. P. sodium chloride. In practical curing, however, the salt employed contains certain impurities, such as calcium and magnesium salts, clay, silica, iron and aluminium oxides, all in varying quantities. Consequently, we have gathered samples of hide salt from various localities. The chemical analysis of these salts is shown in Table XVI. We cannot vouch for the absolute representativeness of these samples, but believe them characteristic.

A difference in the chemical composition of these salts is noticed. Some of them are acid, some alkaline to phenolphthalein. Repeated laboratory experiments indicate that the composition of a salt has a very definite effect upon its diffusing and dehydrating power. This important feature is now being studied and will be reported upon later, after checking by practical experiments. For the present, we would say; depending upon whether a salt is acid, neutral or alkaline in character its curing rate will be rapid or slow.

[4] This JOURNAL, 16, 435 (1921).

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TABLE XV.—Effect of Post-mortem Changes upon Salt Diffusion into Hide

Period of salting	Condition	A Immediate salting	B Salting delayed 4½ hours	Ratio B/A
1 hour	Blood present [1]	1.049 gms. NaCl absorbed	0.261 gms. NaCl absorbed	24.9
1 hour	Blood removed	1.820 gms. NaCl absorbed	1.344 gms. NaCl absorbed	73.8
2 hours	Blood removed	2.170 gms. NaCl absorbed	1.510 gms. NaCl absorbed	69.5

[1] Note that in this case two factors function, both post-mortem changes and blood effects.

TABLE XVI.—Showing Chemical Analysis of Various Salts

	Chicago	New Orleans	Salt Lake salt	Fort Worth	German (Hamburg)	Turks Island	English (Liverpool)	Used salt	San Francisco	South American
Sample No.	1	2	3	4	5	6	7	8	9	10
NaCl	97.06	96.49	96.49	96.79	99.30	96.30	97.78	—	98.79	97.75
CaO	1.43	0.50	0.48	0.43	0.21	1.24	0.50	0.61	0.20	0.64
MgO	0.19	Trace	Trace	0.08	0.04	0.26	Trace	0.11	Trace	0.06
$Fe_2O_3 + Al_2O_3$	Trace	Trace	Trace	Trace	Trace	Trace	—	0.22	—	Trace
SO_3	1.52	0.33	0.35	1.08	0.24	1.414	0.748	—	1.74	0.84
Cl	59.10	59.69	59.69	59.65	60.40	58.11	59.83	—	59.92	60.04
CO_2	Trace	—	—	Trace	—	—	—	—	—	—
H_2O	0.17	0.07	1.13	0.03	0.02	1.27	0.26	0.00	0.20	—
Acidity[1]	1.0	1.0	0.5	1.0	1.0	(8.5)	(4.5)	—	1.0	1.0

[1] Acidity or alkalinity is given in terms of cc. N/10 acid or alkali per 100 grams salt to phenolphthalein. Alkaline salt bracketed.

Nos. 2 and 8 are samples of same salt, 8 having been used previously for salting.

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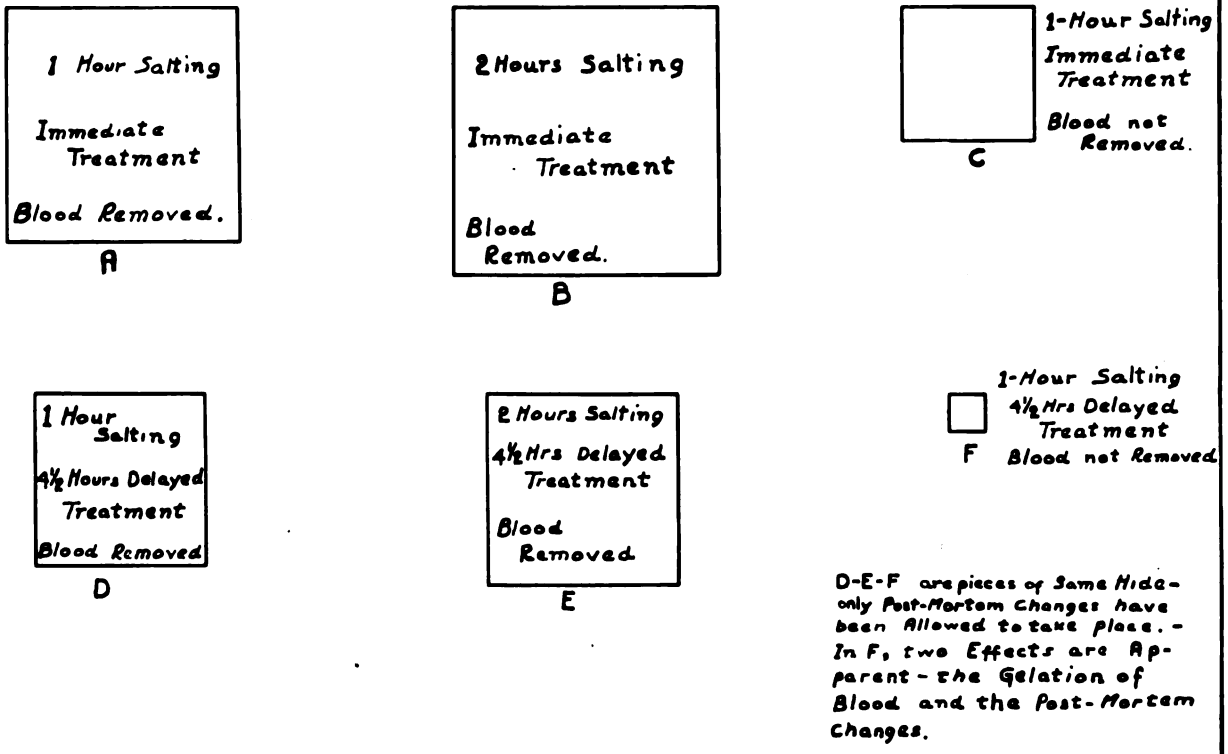
Fig. 9.

Showing Effect of Post-Mortem Changes Upon Salt Diffusion into Hide.



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SUMMARY

We have learned that among the important phases of curing there are:

1. Length of time elapsing between the animal's death and the salting or brining of its hide.
2. Speed of salt diffusion into the hide.
3. Conditions retarding salt diffusion.
   a. Presence and condition of blood.
   b. Post-mortem changes.
   c. Composition of salt.

When hides are properly washed and brined, before salting in pile, we entirely remove the blood and its effects; a maximum salt absorption rate is secured; the effect of post-mortem changes is minimized; salt and iron stains are practically eliminated and, in the end, we have a uniform cure yielding more, thicker and better leather than present curing methods permit.

THE PRACTICE OF HEAVY HIDE CURING*

By George D. McLaughlin and Edwin R. Theis

FROM THE DEPARTMENT OF LEATHER RESEARCH OF THE TANNERS' COUNCIL IN THE UNIVERSITY OF CINCINNATI

The curing of hides and skins represents the first step in both the science and practice of tanning. In studying curing we selected heavy hides, since they offer better facilities for accurate investigation than do light skins; because they are thicker. The principles underlying the curing of each class are the same.

The general methods of heavy hide curing in the United States are as follows. When hides are removed from the carcass they lie in the hide-cellar until the "body-heat" has dissipated; they are then spread, one on top of the other, the flesh side covered with a layer of salt, until a pile of the desired height is reached. The pile is so constructed that part of the brine formed runs away. After a number of weeks the hides are considered cured and are then ready for sweeping, bundling and shipment.

There is no definite rule as to the period of time allowed for the dissipation of body-heat. This depends upon the tempera-

*Read at the Nineteenth Annual Meeting of the A. L. C. A., Bigwin Inn, Ontario, Canada, June 22, 1922.

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ture of the cellar and, in poorly regulated cellars, upon the convenience of the spreading gangs. Usually hides are salted within one to two hours from flaying; sometimes not for six or more.

The temperature of cellars varies; we have found a range of 40° to 90° F.; 50° F. is probably the average.

Sometimes new salt is used, but most often old salt (that which has been already used one or more times) is mixed with new; sometimes all old salt is employed. The old salt becomes mixed with blood and other foreign matter.

There is a weight shrinkage between the blood weight (as the hide leaves the carcass) and the shipping or cured weight. This shrinkage varies. The condition of the hide as to the amount of manure or other foreign matter present on it varies. Its moisture condition varies.

Such is the history of the hide. During the tanning process many perplexing problems arise; hides from the same cellar and of similar selection, weight and take-off may yield quite dissimilar results throughout the tannery, despite every effort to maintain uniform operating conditions. Sometimes the white-weight is high, sometimes low; sometimes the leather yield is high, sometimes low; sometimes the leather is plump, sometimes flat; sometimes hides show many "salt" or "iron" stains, sometimes few. What actual proportions of these discrepancies is due to improper curing it is impossible to state, certainly not all, but certainly some.

The standardization of every tanning process and uniformity of the end product have long been the goal of both tanner and leather chemist. The accomplishment of this end, however, is hopeless when the past history of the raw material is unknown and the influence of the many factors in curing remain a matter of hypothesis. A successful builder must understand foundation construction.

Realizing the truth of these statements and knowing that improvement in and standardization of curing would be profitable to packer and tanner alike, several Packers extended us a cordial invitation to experiment on a large scale in their hide-cellars. It is a pleasure to acknowledge here our debt to them; they enabled us to combine science and practice.

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From the facts learned in our chemical and bacteriological studies we concluded that washing and brining hides before salting (in somewhat the same manner as South American Frigorificos are cured) should be an improvement over present domestic methods. Our conclusions have, indeed, proved to be correct.

By properly regulated washing and brining we control the really determining factors. The blood effects are removed entirely, post-mortem effects are minimized, the most rapid rate of salt absorption is secured, and finally, salt and iron stains are practically eliminated.

Our experimental methods were as follows: As the hide left the carcass it was immediately split into sides. One side was salted within one hour from flaying with all new salt; the other was at once washed with running water, and then brined for twenty-four hours in a 25 per cent sodium chloride solution, then removed, allowed to drain for a few minutes, and then salted down with all new salt. In this splitting procedure, right and left sides were, of course, alternated, so as to secure an equal pate distribution. The sides were run in lots of twenty-five or fifty, the weight when flayed (blood weight) being accurately taken. It will be noted: 1. we have eliminated all question of any inherent differences in hides, since each hide was split into sides; 2. the 'salted' lots were given every possible advantage of prompt salting with all new salt. After six to eight weeks cure the packs were taken up, the various corresponding lots kept intact, and shipped to the tanneries. Each tannery gave to both brined and salted lots their regular process. The lots were all worked through at once; this eliminated any variables due to changes in weather or in hide-house, beam-shop or yard conditions.

Part of the experiments received what might be termed "mellow" beam-house treatment, involving somewhat long soaks, mellow lines and warm water pool, the other part received treatment of the opposite nature; shorter soaks and sharp lines. Anyone having had practical experience with the tanning of Frigorificos knows that their beam-house requirements differ from heavy, domestic hides. The experimental results are as follows:

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1. Shrinkage from Blood to Tannery Received Weight:
   Brined 19.00 per cent.
   Salted 17.86 per cent.
2. White Weight Gain:
   "Mellow" beam-shop treatment.
   Brined stock made 0.5 points less than salted on blood weight.
   Brined stock made 1.2 points more than salted on tannery received weight.
   "Sharp" beam-house treatment.
   Brined stock made 3.8 points more than salted on blood weight.
   Brined stock made 5.5 points more than salted on tannery received weight.

(For example; suppose, in the last case, the white-weight gain of the salted was 120 per cent, the brined made 125.5 per cent).

3. Yard or Pure Leather Gain:

(This was obtained by drying leather out of tan pack with no treatment other than a cold water rinse).

   "Mellow" beam-shop treatment.
   Brined stock made 1.1 per cent more leather than salted, on blood weight.
   Brined stock made 2.7 per cent more leather than salted on tannery received weight.
   "Sharp" beam-shop treatment.
   Brined stock made 1.7 per cent more leather than salted, on blood weight.
   Brined stock made 2.6 per cent more leather than salted on tannery received weight.
4. Finished Sole Leather:
   "Mellow" beam-shop treatment.
   Brined stock made 0.2 per cent more leather than salted on blood weight.
   Brined stock made 1.8 per cent more leather than salted on tannery received weight.
   "Sharp" beam-shop treatment.
   Brined stock made 1.4 per cent more leather than salted on blood weight.

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Brined stock made 2.2 per cent more leather than salted on tannery received weight.

Note: The "Blood Weight" is the proper basis for accurate comparison, since it represents original pounds of hide, and eliminates any complications arising from variations in shrinkage or arbitrarily chosen tare allowances.

Quality of leather: the brined stock receiving "Mellow" beam-shop treatment appeared somewhat depleted in the white, compared with the salted. Throughout the liquors, however, it recovered and the finished leather showed quite fine; plump, firm and quite equal to the salted; if anything it was somewhat thicker and firmer, especially in the flanks. The stock receiving the "Sharp" beam-house treatment showed an unmistakable difference in favor of the brined versus salted. It was very much plumper in the white (note white weight gains) and out of the rockers and each layer it consistently maintained this greater plumpness, as well as in the finished state.

We have already emphasized that in these experiments we purposely gave the brined stock the severest possible test; the comparative salted stock was salted promptly upon cooling, with all new salt. Let us consider briefly what the results indicate. If we judge by leather weight yields alone, the differences found are not startling, although sufficient to amount to a considerable sum in a year's operation. In this connection we must remember, too, that no attempt was made to put a maximum load into the plumper brined stock. If we judge by plumpness and firmness, the brined stock has a decided advantage. If we judge by the comparative number of salt and iron stains (see later paragraph) the brined stock again shows to advantage. Or, if we consider what to our minds is ultimately the most important point of all—*the uniform condition of stock entering our tanneries*,—then brining represents a most promising field of experimentation, both for heavy and light stock. It is futile to expect a tanner to produce a fine uniform, homogeneous run of leather, when his raw material has had an unknown history. The proverb that leather is made in the beam-shop needs revision; the potentiality of a hide or skin is determined in the hide-cellar.

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We have heard much regarding salt and iron stains; they are a constant source of trouble and expense. Much study has been given them by competent investigators, from whose work we know that they probably arise from more than one cause; bacteria, salt impurities and the iron present in blood all playing a rôle.[1] These investigations have led to various attempted remedies such as mixing soda-ash, zinc chloride, calcined soda or sodium sulfite with the curing salt. There is no doubt that benefit, so far as stain removal is concerned, has been derived in certain cases from using these chemicals. There is also no doubt that in using them we may be introducing factors whose effect upon the leather potentiality of the stock is unknown. The removal of the *cause* of disease is the best theraphy. The great bulk of the cause of stains is blood, acting directly or indirectly. When we wash and brine hides we remove the bulk of the cause of stains. This is proved by our own experiments and the recent large scale experiments of others, where it was found that brined stock shows just one-tenth the number of stains compared with salted stock. This one-tenth was made up largely of little spots due to iron and copper present in the salt. We know, also, that stains on Frigorificos are rare.

Summary

In so far as these practical experiments are concerned we find:

1. When heavy hides are properly brined and tanned, they produce more leather from the same original blood weight, than if not brined.
2. Brined hides produce thicker and firmer leather.
3. Brined hides show a minimum of salt and iron stains.
4. Brined hides require special beam-house treatment.
5. Improper washing or brining may be harmful rather than beneficial; the two processes must be intelligently executed.
6. Brining offers a means of standardizing curing.

A uniform, standardized curing of raw stock will be valuable to the packer who produces the hide, to the tanner who tans it, and to the public which wears and pays for it.

[1] See: Abt., *La Halle aux Cuirs*, July 28, 1912 (Reprinted This Journal 7, 492 (1912); *Collegium*, 1912. p. 388-408; *Ibid*. 1913, p. 204, 206, 439. Becker: *Collegium*, 1912, p. 408. Paessler, *Ledertechn Rundschau*, 1912, p. 137; *Ibid*, 1921, p. 169. Yocum, This Journal, 8., 22 (1913).

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THE DISTRIBUTION OF GREASE IN LEATHER *

By Lloyd Balderston

It has long been known that in leather oiled or curried by the usual methods, the percentage of grease in different parts of the hide varies widely. This was well shown in Mr. Small's report last year of the work of the committee on sampling leather. This difference in what may be called the horizontal distribution of grease is believed to be due to the varying texture of different parts of the hide, the more loose and flexible parts taking more grease.

It is also well known that if a piece of leather be split into several layers, the percentage of grease in the middle portions will in general be found to be less than in the outside layers. Very often, also, the percentage in the grain will be higher than in any other part. Distribution with reference to the thickness of the leather may be called vertical distribution. The following experiments were tried in an effort to learn what relation the vertical distribution of grease has to the method of currying.

A lot of pieces were heated, swabbed with hot grease on the flesh side only, and allowed to lie in pile for some hours. In the table which follows this lot is marked A. When finished, these pieces showed on being split into three parts of equal thickness 17 per cent grease in the grain, 2.5 per cent in the middle and 8.5 per cent in the flesh. A second lot (B) were treated in the same manner and when finished split into four equal layers. These in order from grain to flesh showed 19, 5, 3 and 9 per cent respectively.

It was thought that the high percentage in the grain might be in part due to absorption from adjoining pieces as they lay in pile. In the next experiment small pieces were used and special care taken that no grease should be allowed to get on the grain side. Four of these were warmed and swabbed on the flesh with melted grease. One was kept at 60° C. overnight, the others in a moderately warm place. Next morning not all the grease had penetrated in these three, so they were placed in the

*Read at the Nineteenth Annual Meeting of the A. L. C. A., at Bigwin Inn, Ontario, Canada, June 22, 1922.

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oven at 60° just long enough for all the grease to go in. All were now split into three layers and grease determined. The grain of that which was kept at 60° overnight had 27.2 per cent grease, middle 4.6 per cent and flesh 8.3 per cent. The other three pieces were worked together, the grain giving 13.5 per cent, middle 5.3 per cent and flesh 17.2 per cent. One piece from the same part of the same hide which had received no grease was split and examined, showing 7.2 per cent in the grain, 0.8 per cent in the middle and 2.3 per cent in the flesh.

Three other pieces were now treated in the same manner, having previously been heated to about 60 degrees, so that the grease penetrated at once. They were then set aside at room temperature overnight, split and examined with the following result: grain, 9.2 per cent; middle, 6 per cent; flesh, 20.6 per cent. A piece soaked 1 hour in a 10 per cent emulsion, then dried, split and extracted gave 12.5 per cent in the grain, 6 per cent in the middle and 11.8 per cent in the flesh. All the foregoing results are collected in Table I.

TABLE I.

	Grain	Middle	Flesh
Swabbed on flesh, piled, A	17	2.5	8.5
Swabbed on flesh, piled B	19	5 3	9
Swabbed on flesh, heated 14 hours	27.2	4.6	8.3
Swabbed on flesh, heated till grease penetrated	13.5	5.3	17.2
Hot swabbed on flesh; immediate penetration, stood 14 hours cold	9.2	6	20.6
One hour in 10 per cent emulsion, dried	12.5	6	11.8

A set of seven pieces one inch wide, cut from the shoulder ends of seven bends of rough oak leather were now split into seven layers and examined. The layers are numbered from 1 to 7, grain to flesh. These bends had been oiled off in a drum in the usual manner. Results are given in Table II.

TABLE II.

Layer	Av. thickness inches	Total weight grams	Moisture	Grease per cent	Grams grease in sample
1	0.023	49	11.5	5.44	2.416
2	0.016	39	12.8	4.30	1.677
3	0.020	58	14.5	2.24	1.300
4	0.022	64	14.2	1.79	1.246
5	0.016	38	13.1	2.28	0.866
6	0.045	123	13.4	3.44	4.231
7	0.029	80	15.0	8.00	6.400
Total		451			18.136
Average per cent grease			4.02		

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A careful examination of these results shows that there must be some other cause of variation than that which has been mentioned as the probable reason for the varying horizontal distribution of grease.

It is well known that when leather or other porous material is saturated with a solution of some substance for which it has no chemical affinity, and then allowed to dry, the liquid as it flows from the interior toward the surface brings with it the dissolved material, which thus tends to accumulate on and near the surface. If we were here dealing only with oil in emulsion, a similar explanation might be offered. The most striking instance of accumulation of grease in the grain in the above experiments was in the case of a piece which had not been wet after it was stuffed, so it is hard to see how water could have been an agent in the transfer of grease to the grain side.

It may be fairly assumed that the piece which was kept at 60° for 14 hours after oiling had reached an equilibrium condition. Assuming that the piece which was examined without oiling is a fair sample, the grain of the other had risen from 7.2 per cent grease to 27.2 per cent, a rise of 20 per cent, all this having come through the leather from the flesh side. It seems reasonable to suppose that the larger appetite of the grain for grease is due to its close texture, which gives it a greater capillary pull than that exerted by the coarser and looser fibers in the middle. A piece of leather with three times as much total grease, saturating the whole thickness, would probably show no such wide variation in vertical distribution.

LABORATORY OF J. E. RHOADS AND SONS, WILMINGTON, DEL.

ABSTRACTS

Gambier.* *Journal R. S. A.*, 70, 523 (1922). Gambier is planted from seeds in nurseries until the plants are 4 to 5 inches high when they are planted out 6 to 10 feet apart.

A gambier estate is generally spread over a large area, in which there are patches of planted ground and the estate usually aggregates 70,000 bushes; in addition to the planted area large timber reserves are necessary to supply firewood.

* Extracted from "Notes on Sarawak Trade," published by the Committee for Agricultural and Forest Exhibits, Malaya-Borneo Exhibition.

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Gardens are weeded twice a year by hand until the young plants are two years old, after which period they are weeded by hoe.

Gambier is prepared from the leaves and young shoots of the bush, which are gathered every six months after the second year. The 70,000 bushes are attended to by seven men, including those engaged in the preparation of the gambier; of these seven men, two are employed weeding, two gathering, one procuring firewood, one in charge of the cooking process and one general coolie; the work is extremely hard and scale of wages low, especially when the gambier market is low, when it is customary to reduce wages.

If a plantation is not worked regularly the plants are ruined, so gathering takes place even if the price of gambier is so low that the owner incurs a loss on the manufacture. When gathering does not take place regularly the leaves turn red, the young shoots harden and production of young shoots ceases.

Cutting the leaves commences at daylight and continues until 8 o'clock, the weeders assisting the gatherers in bringing the leaves to the factory; at 10 o'clock the gatherers have to go out for leaves for the afternoon cooking, returning about 1 P. M. These gatherers do not assist in the cooking process although they cut the leaves with choppers to prepare for cooking. About 3½ piculs of leaves, etc., are gathered at one time.

Leaves on the main stem are taken first, then the leaves and shoots of the side branches, leaving the upright shoots to produce future supplies.

Harvesting from each takes place once in six months, the gatherers moving from patch to patch of planted area over the whole estate; some of these gardens are often two miles from the factory.

The gathered leaves and shoots are taken to the factory, chopped up, and put into a large copper, which has sides built up with wood, set over a large furnace fed by firewood.

The cuttings are boiled for three hours, being continually turned over with a special wooden instrument having five long prongs; when cooked they are removed by means of a large three-pronged fork and put into a trough (jalor) above, which is set at an incline towards the cooking copper; after the larger leaves have thus been removed the smaller broken pieces are strained by means of a rattan strainer. The cooked leaves, etc., are washed with cold water; the first washings, still of a dark brown color, run back into the cooking apparatus; the weaker washings are led off through a small trough into a receptacle fixed next to the main copper. These weak washings are transferred to the main copper for the next washing, the new leaves, etc., being added to it.

The liquid in the main copper is now cooked for a further two hours, after which it is removed to small tubs to cool.

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If this liquid is left to cool the gambier will not solidify; in order to attain this result a short stick is inserted into the tub at an angle and coolies immerse their hands in the warm liquid and rub up and down the stick with a spiral motion until the color of the liquid becomes lighter. During this process it thickens; after the liquid has been "worked" for about 15 minutes it is left, and when quite cold it of the consistency of cheese.

When it is quite cool the gambier is removed from the tubs and cut up into sections after which it is dried in the sun for one day and then placed in the rafters of the factory for smoking.

Also after cooking, the liquid may be put into tubs as before, and about 4 tahils of rice bran, which has previously been fried and passed through a sieve, is added; this mixture is "worked" as before and just before becoming solid it is poured into a mould made of wood. The mould is set on a mat and on all inside casings of it are lines to mark the moulded gambier ready for cutting. When the gambier is set, the side of the mould is opened and the block is cut up into cubes by means of thread.

The wet cubes are placed in a bamboo tray and left to dry for one day, after which they are placed in the rafters of the factory to be smoked; this process takes about nine days.

Dressing Australian Wool Skins. *Australian Lea. Jour.*, through *Color Trade Jour.*, **10**, 245 (1922). The dressing of wooled sheepskins was largely developed during the war, and is now an established line with many leather dressers. The methods are simple, and the goods are used for a variety of purposes. The class of skins processed should be sound, plump pelts, taken, if possible, just after shearing; and the following directions will give satisfactory results:

The most suitable skins are fresh or dry salted stock. Soak for 24 hours in clean water, to which has been added one-half per cent carbolic acid, not only as a disinfectant, but to prevent the wool from slipping during the scouring operation, the acid having a slight tanning action. If preferred, 1 per cent alum can be substituted for the acid. Sun dried skins should be soaked for 24 hours, broken over the beam, and re-soaked until thoroughly soft and the flesh well broken. After draining from the soaks the goods are ready for fleshing. Any of the standard makes of fleshing machines are quite satisfactory, provided care is taken in adjusting the machines correctly.

The best method of scouring or cleaning the wood is by the three-mangle system. The mangles are similar to laundry mangles, with two rollers under a single roller, the top roller touching the bottom rollers, thus obtaining a double action. These machines are fixed over 100-gallon vats, and driven by power. The goods are folded from neck to butt, wool out, and placed in No. 1 vat, then passed through the rollers until the wool is fairly clean, thrown into No. 2 vat, and the process repeated

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until quite white and clear. Rinse through No. 3 vat, and the process is completed. The materials and quantities used for scouring are as follows:

Dissolve 30 pounds of textile soap in 50 gallons of water; if possible, in a steam-jacketed pan. Fill up vats Nos. 1 and 2 with water heated to 98° F., and add 9 gallons of the soap solution to each vat, together with 10 pounds of soda ash. Vat No. 3 is filled with water only, to clear the wool of soap.

Should the wool be too long for the purpose required it is advisable at this stage to shear to the required length. This can be done, after the goods have drained for one hour, on a table sloping away from the operator, with a sheep-shearing machine, care being taken not to cut the pelt. The wool, being scoured, is more valuable, and the saving in tanning materials is considerable by taking off any surplus wool.

The tanning process can be carried out in a drum, revolving at not more than twelve revolutions per minute, or in paddles. A tannage that will give a full, supple leather, with the wool clean and nearly white, is obtained by tanning in a liquor composed of 10 per cent alum, 10 per cent salt, 10 per cent cube gambier on drained weight of goods. Drum or paddle for four hours at 104° F.; then allow the goods to lie in the liquor overnight. Run for one hour the following morning; then lay on horses to drain for 24 hours. Run through mangle or burring machine to clear the wool of tanning materials, using water heated to 70° F.; then, if possible, shake in a hydro-extractor. When in a "sammed" condition set out lightly on setting machine, and hang up to dry.

When the goods are dry spread in a cool place for a few hours; then pile in damped sawdust in pairs, pelt out, until damped through. Lay in piles, covered over, for 24 hours, and the goods are ready for staking. Stake by hand or machine. Staking by hand is usually done in a perch with a crutch stake. After staking, the goods are hung up in a warm room to air off, re-staked, and the flesh side finished off or "faced up" on a buffing machine or emery wheel.

Skins required for leather waistcoats, motor gloves, slippers, and so forth, can be stained on the flesh side to the desired color, dried off, lightly staked with a dull knife, and brushed up with a hard brush to raise the "nap."

A "Micro-Kjeldahl" Method of Determining Nitrogen. By A. R. LING and W. J. PRICE. *J. S. C. I.*, **41**, 149T (1922). After an experimental investigation of various methods suggested for determining small amounts of organic nitrogen in small samples the following method was adopted:—An accurately weighed portion of the substance containing 1-0.1 mmg. of nitrogen is introduced into a hard glass boiling tube together with 1 gram of dry potassium sulphate and 0.02 gram of anhydrous copper sulphate, 8 cc. of concentrated sulphuric acid is then added and two drops of 2.5 per cent platinum tetra-chloride solution. A small funnel is placed in the mouth of the tube, and the contents are boiled gently until the liquid is colorless. In the case of carbohydrates this

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occupies about 1 hour. The liquid is then allowed to cool, about 15 cc. of distilled water added, and the diluted liquid boiled to expel any sulphur dioxide. When cold the liquid is introduced into a 300 cc. distilling flask fitted with a tap funnel and connected with a Liebig's condenser by the side tube. The further end of the condenser is fitted with an adapter, the end of which dips into about 50 cc. of water, contained in a graduated 250 cc. flask. A few pieces of freshly ignited porous porcelain, free from nitrogen, are added to the flask to prevent bumping, and a small strip of litmus paper. Sodium hydroxide of 40 per cent strength is added through the tap funnel until the contents of the flask are alkaline. Distillation is now commenced and continued until all the ammonia has passed over. It is necessary to distil about 100 cc. To the distillate 1.5 cc. of 40 per cent sodium hydroxide is added, and then 5 cc. of the Nessler reagent, the contents of the flask being well shaken after the addition of the sodium hydroxide and of the Nessler reagent. The liquid is then made up to 250 cc.

A stock solution of ammonium sulphate is prepared containing 4.716 grams of that salt and 200 cc. of N/1 sulphuric acid (to inhibit the growth of micro-organisms) in one litre. This solution contains 1 mg. of nitrogen per cc. One cc. of this solution is added to about 150 cc. of water in a 250 cc. graduated flask. To this is added 1.5 cc. of 40 per cent sodium hydroxide solution, and 5 cc. of the Nessler reagent, the liquid being well shaken and made up to 250 cc.

After allowing 5 minutes in order that the color may develop, 10 cc. portions of each of the two solutions—the Kjeldahl and the standard—are introduced into two small flat-bottomed tubes of colorless glass. The dimensions of the tube may be conveniently 9.3 cm. in length and 1.5 cm. in diameter. The tubes are placed on a clean sheet of white paper and the tints of their contents compared, by viewing the surfaces. From the darker of the two solutions quantities are withdrawn by means of a pipette graduated in 0.01 cc. until the tints are equal. The solution from which a portion has been withdrawn is then again made up to 10 cc. with distilled water and the comparison again made. It may then be necessary to make a further adjustment, but the final comparisons must always be made on equal depths of the two liquids.

Action of Soap on Chrome Leather. By IMMENDÖRFER and PFAHLER. *Chem. Umschau*, **29**, 73 (1922); *J. S. C. I.*, **41**, 303A (1922). Experiments to determine the action of soap on chrome-leather showed that the alcoholic extract of two-bath leather consists of 63 to 85 per cent free oleic acid. In the case of single-bath leather the alkali of the soap was found to have penetrated into the leather to a certain extent. The more completely single-bath leather has been de-acidified the more free oleic acid can be extracted from it with neutral alcohol.

Formaldehyde Tannage. By A. M. HEY. *J. S. L. T. C.*, **6**, 131 (1922). The author describes a series of experiments on tanning ox hide with formaldehyde wherein the p^H values of the hide and tanning solutions were estimated before and after tanning. It appears that the tannage of hide

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with formaldehyde can be carried out to completion, provided the pelt is kept in such a condition that its p^H is on the alkaline side of the isoelectric point of collagen which is about p^H 4.8. In solutions on the acid side the tannage is incomplete, also if too high a hydroxl ion concentration obtains the tannage is incomplete. Under such conditions a hard and horny leather is obtained which is credited to excessive plumping and a tannage of the plump surface which forms an impermeable external layer. The use of concentrated solutions of alkali carbonate is explained by the dehydrating influence of the large excess of salts and ions in the solution. G. W. S.

The Factors Influencing the Plumping of Hides in Tan Liquors. By W. R. ATKIN. *J. S. L. T. C.*, 6, 138 (1922). A general discussion of some of the various factors which influence the plumping of hides in tan liquors. It is stated that the work of Procter, Wilson and Loeb has demonstrated conclusively that the swelling of proteins in acid or alkaline solutions is due to the formation of salts of the type gelatin- chloride or sodium gelatinate which ionize and tend to swell the protein. Chemical control of swelling is difficult because of the several factors involved.

The direct swelling method of control yields useful results but it must be remembered that the swellings are only relative and depend on the amount of hide powder used, the size of the hide powder particles and to a certain extent on the temperature and that there is no definite relationship existing between the figures obtained for hide powder swelling and the swelling of pieces of hide in similar solutions because the cohesion factor is very different in the two cases. Whilst it is an exceedingly useful control for suspender liquors the swelling method does not afford much help in indicating how the liquors may be regulated to produce better results. The lime water titration only indicates the total amount of acid in the liquor and gives no indication of the swelling power. Hydrion measurements yield valuable information but take no account of the repressing action of neutral salts and the reduced swelling power due to combination between hide and tannins.

It is therefore suggested that the best method of controlling the early liquors in a heavy leather tannery is to employ the lime water method, hydrogen ion determinations and also the direct swelling method for each pack of hides, tabulate the results and note the result of the finished leathers. G. W. S.

Histological Examination of Hide. By L. KRALL. *Le Cuir*, 11, 185-7 (1922). A brief review is given of work on the preparation of hide for histological examination and the possible value of such studies in the control of tanning operations is emphasized. Since the usual methods for fixation, dehydration, embedding and so on require too much time for control work, the author has tried the freezing method for preparaing sections of hide with success, being able to secure sections stained and ready for microscopic examination in 3 hours or less . The freezing effect is obtained by the evaporation of a stream of compressed gas played on the sample mounted on the microtome stage. Fixation is not

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necessary, though with some samples when not fixed the formation of crystals of ice in the interior causes ruptures. If circumstances permit, it is better to fix the sample with a bath of 5 per cent formaldehyde for one-half hour, or with Muller's solution provided salts of chrome will not interfere. R. W. F.

Formaldehyde in the Leather Industry. By G. DESMURS. *Bourse aux Cuirs de Bruxelles,* June 9, 1922, 517-23. The well known properties and uses of formaldehyde in the tannery are described at considerable length. Several detailed formulas are given. For white sheep and lambskin leather a tan liquor is made up of 13.5 kgs. soda crystals in 45 to 65 liters of water to which are added 7.25 kgs. 40 per cent formaldehyde. These quantities suffice for 200 kgs. of white weight. After tanning, which is done by adding the alkaline-formaldehyde solution in portions of 4.5 liters at a time, neutralization is effected with 2.75 kgs. ammonium sulphate.

In vegetable tanning plumping is fixed by a dilute solution in the proportion of 2 liters of 40 per cent formaldehyde in 10 hectoliters of water. As a pretannage for heavy leathers 1.25 kgs. of formaldehyde per 100 kgs. of white weight is recommended; for fixing the grain 0.5 per cent on white weight is used. R. W. F.

The Manufacture of Tanning Extracts. By G. CHEVRAUX. *Le Cuir,* 11, 208-9 (1922). A general description is given of a small unit capable of extracting about 40 tons of chestnut wood or 30 tons of mimosa, myrobalam, valonia and the like per day. This unit is of very economic construction, and yet very efficient and can be moved at little expense. The latter is a desirable feature in view of the exhaustion of large wood areas. The unit can be constructed at a cost of less than 500,000 francs and can be operated by two men.

A special installation for rich materials such as mimosa and valonia has been devised making possible an automatic extraction, giving directly an extract of 25° Bé, and with a consumption of steam of from 5 to 7 times less than required by the present types of installation. The extraction is also very complete. The advantages of such an equipment to the tanner who extracts for his use such materials are pointed out. R. W. F.

The Relation between Hydrolysis and Adsorption V. By W. MOELLER. *Zeitsch. Led. u. Gerb. Chem.,* 1, 161 and 183 (1922). A study of the hydrolysis of gelatin by acids using the same procedure as that adopted for previous work on hide powder, namely, using 4.4 grams of gelatin powder to 100 cc. of solutions of various strengths of acids, allowing to stand after mixing for different periods of time and determining nitrogen in solution by the Kjeldahl method. Gelatin contains a considerable amount of hydrolysed gelatin and it distinctly shows hydrolysis in distilled water . The water values of this particular sample, 4.4 grams of powdered gelatin and 100 cc. of water, showed in 1 hour 28.69 per cent, 1 day 37.33 per cent, 2 days 37.87 per cent and 5 days 39.65 per cent of the gelatin in the filtrate. Results with hydrochloric, acetic, lactic and

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butyric acids are given without the use of kaolin in the filtration, and since hydrolysis of gelatin proceeds first as a breaking down of the gelatin complex into smaller molecular complexes which are colloidally dispersed thence into molecules and finally cleavage products of the molecules, the two latter would exist in true solution, and in order to differentiate between that portion of the gelatin which is in colloidal dispersion and that in molecular dispersion a set of experiments similar to the above was run but using kaolin in the filtration. A new sample of gelatin was used in this portion of the work which showed a different water value and gave results that were generally higher than those obtained in the first portion of the work. The results as a whole seem to be very erratic and do not seem to justify more than the conclusion that hydrochloric acid hydrolyses gelatin to a much greater extent than the organic acids. Although the author frequently alludes to the sources of error in this work he does not hesitate to draw conclusions which should, in the opinion of the abstractor, need a little firmer foundation. G. W. S.

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NOTICE

The Council of the Association has invited members to express their views in the JOURNAL upon the question as to how "purity" of tanning materials should be calculated, whether this should be expressed by the relationship between the total solids and tannin or the soluble solids and the tannin.

H. C. Reed, *Secretary*

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COUNCIL MEETINGS

A meeting was held at the close of the annual convention at Bigwin Inn, Canada on June 23rd, with the following members of the Council present: C. C. Smoot, III, J. S. Rogers, H. C. Reed, G. D. McLaughlin, G. W. Schultz and C. R. Oberfell. It was decided to hold a meeting of the Council in New York City as soon as the stenographic report of the annual convention was ready for use.

A meeting of the Council was held in New York City on July 24th, with the following members present: C. C. Smoot, III, J. S. Rogers, H. C. Reed, G. W. Schultz and C. R. Oberfell.

The recommendation that the Official Method of Tannin Analysis, Section 12-A Non-Tannins, be changed to include the method for Rapid Washing of Hide Powder (see Committee Report, This Jour. **17**, 210, 1922) was approved and will be submitted to the vote of the membership.

It was voted that the provisional method for analysis of Chrome Leather—(a) Borax Glass Fusion—should be submitted to the vote of the Association with the view of making the same official.

It was voted that the members of the Association should be requested to express their views in the JOURNAL as to whether "purity" of materials containing tannin should be expressed by the relationship between the total solids and the tannin, or the soluble solids and the tannin.

The Council determined upon the following as proper subjects for committee work for the ensuing year and selected the various chairmen as indicated:

Determination of Moisture in Leather..... F. P. Veitch
Determination of the Water Soluble in Leather. G. W. Schultz
Determination of the Sugar Content of Leather.. R. W. Frey
Determination of Sugar in Extracts..... R. W. Frey
Chrome Leather Analysis ..... L. Balderston
The Direct Measurement of the Plumping Power of Tan Liquors..... R. W. Hart
The Color Measurement of Vegetable Tanning Solutions..... T. Blackadder
Synthetic Tanning Materials..... T. Blackadder

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An Alternative Filter Paper for Soluble Solids Filtration.....
L. E. Stacy
Comparative Tannin Analysis with Revision of Official Methods
H. C. Reed
Testing of Dyestuffs used on Leather..... A. A. Claflin
Elucidation of the Details of the Method for the Determination of Free Sulphuric Acid in Vegetable Tanned Leather..
Miscellaneous Methods for the Analysis of Materials Used in the Tannery .....F. H. Small

The following problems were selected for research work and the members designated invited to participate, but the Council welcomes research on these problems by other members of the Association:

The Determination of the Penetrating Value of Tan Liquors
R. O. Phillips
The Determination of Oils and Greases in Leather..L. Balderston, A. C. Orthmann, C. W. Reilly, F. P. Veitch
The Determination of Free Sulphuric Acid in Vegetable Tanned Leather ..... R. W. Frey, S. Kohn, T. J. Mosser
The Determination of the Astringency of Tan Liquors.....
H. C. Reed
The Effect of a Definite Hydrogen Ion Concentration upon the Analysis of Tannin Extracts by the Official Methods
T. J. Mosser

H. C. Reed, *Secretary*

NOTES ON HIDE SOAKING EXPERIMENTS

By B. S. Levine

Received June 9, 1922

The experiments recorded below were undertaken by the writer with the view to finding a method for soaking hides which would result in a minimum loss of hide substance, and which, if possible, would eliminate the prolonged process of dehairing, thus saving both time and chemicals. At the present the writer's time is entirely given to the study of chemo-physiological problems of a medical character and he is unable to continue the work on hide soaking. However, the results thus far obtained are sufficiently indicative and encouraging to justify their publication. For lack of time no reference to literature is made, and the paper is written in as brief a form as possible.

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Briefly stated the method was as follows: Pieces of hide of varying weights were soaked under "Normal," "Aerobic," and "Anaerobic" conditions in one-half gallon E-Z seal glass jars containing 1,000 cc. of tap water. The "Normal" condition was attained by allowing the jars to stand open and undisturbed; the "Aerobic" condition was attained by passing a continuous stream of air through the filled jars; the "Anaerobic" condition was at first attained by pouring a layer of mineral oil over the surface of the water. Such a procedure of anaerobiasis possesses considerable disadvantages and had to be given up. The final procedure was as follows: Carbon dioxide, freshly generated and passed through several waters to free it from mineral acid, was passed slowly through the filled jars until it completely replaced the air from over the surface of the water. This was determined by applying a burning match to the mouth of the jar. The jars were then sealed and left undisturbed for the desired period of time. The levels reached by the water in every case were marked on the outside of the jars by a wax pencil, and evaporation was replaced. Thus, the work was carried out in all cases on definite volumes. After opening the "Anaerobic" jars for the purpose of removing a volume of water for the determination of nitrogen in solution, they were refilled with carbon dioxide as described above, sealed, and again left undisturbed for a period of time.

The first series of experiments consisted of two sets containing pieces of hide weighing 100 and 400 grams respectively. Set I of the 100-gram hide pieces was as follows: Jar A-Aerobic; Jar B-Normal; Jar C-Anaerobic. The pieces of hide were freed from superficial dirt by washing them in running tap water. They were then placed in the jars and left standing for about one hour. The jars were then sealed, shaken vigorously one hundred times, a quantity of the liquid taken out from each, filtered through ordinary filter paper, and 20 cc. run into each of three Kjeldahl flasks for nitrogen determinations. The triplicates taken from Jar A were marked respectively 151, 152, 153; those taken from Jar B- 154, 155, 156; those from Jar C- 157, 158, 159. Their nitrogen content was as follows:

151—.00112	154—.00028	157—.00042
152—Lost	155—.00014	158—.00028
153—.00126	156—.00028	159—.00042

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After one day of soaking the nitrogen content per 20 cc. was again determined and found to be as follows:

151a—.00126	154a—.00084	157a—.00140
152a—.00126	155a—.00084	158a—.00140
153a—.00140	156a—.00079	159a—.00126

After two days' soaking the jars were thoroughly shaken, samples of liquid taken out from each, plated out and incubated under normal conditions at room temperature to determine the number of bacteria per cc. in each of the jars. At the end of 24 hours the counts were as follows:

Jar A—Aerobic	—	8,500,000
Jar B—Normal	—	1,800,000
Jar C—Anaerobic	—	400,000

After three days' soaking the nitrogen content per 20 cc. of liquid was again determined and found to be:

151b—.00196	154b—.00140	157b—.00168
152b—.00168	155b—.00140	158b—.00168
153b—.00168	156b—.00140	159b—.00168

The following observations were made: Fluid drawn from jar "A" after filtering was markedly turbid, that from jar "B" less so, and that from jar "C" was practically clear.

After four days' soaking bacterial counts as described above were again made and found to be:

Jar A—Aerobic	—	100,000,000
Jar B—Normal	—	20,000,000
Jar C—Anaerobic	—	6,000,000

After five days' soaking the nitrogen per 20 cc. of fluid was as follows.

151c—.00308	154c—.00630	157c—.00210
152c—.00294	155c—.00630	158c—.00224
153c—.00280	156c—.00630	159c— Lost

The following observations were made:

Jar "A"—fluid filtered with difficulty and was turbid after filtration.

Jar "B"—fluid filtered well, but remained somewhat turbid.

Jar "C"—fluid filtered well, and was clear.

On the same day samples were plated out for bacterial counts and incubated for 48 hours. The counts were as follows:

Jar "A"—Aerobic	—	250,000,000
Jar "B"—Normal	—	55,000,000
Jar "C"—Anaerobic	—	30,000,000

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Seven days from the start of the experiment the nitrogen content per 20 cc. was as follows:

151d—.00420	154d—.01317	157d—.00448
152d—.00420	155d—.01359	158d—.00420
153d—.00420	156d—.01345	159d—.00420

The following observations were made:

Jar "A"—opened dead; hide sank; fluid clear before filtering.

Jar "B"—opened with some explosion; hide sank; fluid was dirty and turbid before filtering.

Jar "C"—opened with an explosion; hide floated; fluid very turbid.

Ten days after the start of the experiment the nitrogen per 20 cc. of fluid was as follows:

151e—.02914	154e—.01793	157e—.01065
152e—.02872	155e—.01765	158e—.01051
153e—.02886	156e—.01779	159e—.01079

The following observations were made:

Jar "A"—Yellowish and very turbid.
Jar "B"—Somewhat muddy, gray and turbid.
Jar "C"—Water white and only slightly turbid.

On the same day samples were plated out incubated for 48 hours, and counted with the following results:

Jar "A"—Aerobic	—	800,000,000
Jar "B"—Normal	—	50,000,000
Jar "C"—Anaerobic	—	25,000,000

Set II of the 400-gram hide pieces was as follows:

Jar "D"—Aerobic, nitrogen triplicates marked respectively 160, 161, 162.

Jar "E"—Normal, nitrogen triplicates marked respectively 163, 164, 165.

Jar "F"—Anaerobic, nitrogen triplicates marked respectively 166, 167, 168.

The nitrogen content per 20 cc. of fluid at the start of the experiment was:

160—.00126	163—.00112	166—.00126
161—.00126	164—.00112	167—.00112
162—.00112	165—.00098	168—.00112

After one day of soaking the nitrogen per 20 cc. was as follows:

160a—.00364	163a—.00392	166a—.00462
161a—.00350	164a—.00432	167a—.00434
162a—.00350	165a—.00420	168a— Lost

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Two days after soaking, the jars were thoroughly shaken, samples taken out from each, and plated out under normal conditions at room temperature to determine the number of bacteria per cc. in each. After incubation, the counts per cc. were as follows:

Jar "D"—Aerobic	—	8,600,000
Jar "E"—Normal	—	6,000,000
Jar "F"—Anaerobic	—	650,000

Three days after soaking, the nitrogen content per 20 cc. was:

160b—.00532	163b—.00715	166b—.00686
161b—.00546	164b—.00743	167b—.00729
162b—.00532	165b—.00729	168b—.00715

The following observations were made: Fluid drawn off for nitrogen determination from jar "D" was very turbid after filtering; that from jar "E" was markedly turbid, and that from jar "F" was almost clear. Fluid from "D" filtered very slowly.

Four days from start of the experiment, the bacterial counts were

Jar "D"—Aerobic	—	150,000,000
Jar "E"—Normal	—	65,000,000
Jar "F"—Anaerobic	—	30,000,000

Five days from the start of the experiment, the nitrogen per 20 cc. was:

160c—.01459	163c—Lost	166c—.02130
161c—.01443	164c—.03741	167c—.02130
162c—.01471	165c—.03713	168c—.02073

The following observations were made:

Jar "D"—Fluid filtered with great difficulty, and was turbid.

Jar "E"—Fluid filtered with less difficulty and was somewhat clearer.

Jar "F"—Fluid filtered well and was slightly turbid.

On the same day samples were plated out for bacterial counts and incubated for 48 hours. The counts were as follows:

Jar D—Aerobic	—	275,000,000
Jar E—Normal	—	150,000,000
Jar F—Anaerobic	—	52,000,000

Seven days from start of the experiment, the nitrogen content per 20 cc. was as follows:

160d—.05930	163d—.08322	166d—Lost
161d—.05916	164d—.08294	167d—.06010
162d—.05930	165d—.08280	168d—.06010

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The following observations were made:

Jar "D" was very turbid, and opened dead. Hide sank to the bottom.

Jar "E"—Fluid was reddish before filtration, dirty and very turbid. Jar opened with violent explosion. Hide was of a very milky white appearance and floating.

Jar "F" was rather turbid before filtering. Jar opened with violent explosion. Hide was floating.

Ten days after the start of the experiment, the nitrogen content was as follows:

160e—.08336	163e—.12076	166e—.10718
161e—.08574	164e—.12216	167e—.10746
162e—.08770	165e—.12133	168e— Lost

The condition of the fluids was:

Jar "D"—Extremely turbid.
Jar "E"—Very turbid.
Jar "F"—Yellowish red and considerably turbid.

Plated on the same day, and incubated for 48 hours and counted with the following results:

Jar "D"—Aerobic	—	2,000,000,000
Jar "E"—Normal	—	150,000,000
Jar "F"—Anaerobic	—	45,000,000

The second series of experiments consisted of three sets containing pieces of hide weighing 100, 200, and 400 grams of hide respectively. Set I of the 100-gram hide pieces of the second series was as follows:

Jar "G"—Aerobic, nitrogen duplicates	—	Nos. 133, 134
Jar "H"—Normal, nitrogen duplicates	—	Nos. 135, 136
Jar "I"—Anaerobic, nitrogen duplicates	—	Nos. 137, 138

The procedure in this case was essentially the same as previously described. The nitrogen content per 20 cc. of fluid at the start of the experiment was:

133—.00056	135—.00070	137—.00154
134—.00056	136—.00084	138—.00140

The following day the nitrogen content per 20 cc. was:

133a—.00196	135a—.00252	137a—.00336
134a—.00210	136a—.00238	138a—.00350

Two days from the start of the experiment:

133b—.00252	135b—.00294	137b—.00378
134b—.00252	136b—.00308	138b—.00378

Three days from the start of the experiment:

133c—.00322	135c—.00336	137c—.00406
134c—.00322	136c—.00350	138c—.00406

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Five days from the start of the experiment:

133d—.00546	135d—.01023	137d—.00504
134d—.00560	136d—.01023	138d—.00504

Six days from the start of the experiment:

133e—.00827	135e—.02087	137e—.00560
134e—.00613	136e—.02073	138e—.00574

Seven days from the start of the experiment:

133f—.01037	135f—.03250	137f—.00658
134f—.01051	136f—.03264	138f—.00672

The following observations were made at the end of the experiment:

Jar "G"—after shaking opened dead; liquid was very turbid, and the hide sank to the bottom.

Jar "H"—after shaking opened with violent explosion; liquid turbid, and the hide floating.

Jar "I"—after shaking opened dead; liquid was somewhat turbid, and hide floating.

The condition of the hide was as follows:

Jar "G," (Aerobic)—Hair removed with ease. The grain was considerably affected, though no holes were eaten through the hide.

Jar "H" (Normal)—The hair removed with ease. The hide was of a milky white appearance. Holes were eaten through the hide in several places. The grain was extensively affected. Generally the hide presented a picture characteristic of one thoroughly decomposed.

Jar "I" (Anaerobic)—Hair removed fairly easily. Hide was of a normal color. Both, grain and flesh sides remained entirely unaffected.

Set II of 200-gram hide pieces of the second series was as follows:

Jar "J" (Aerobic)	nitrogen duplicates,	Nos. 139, 140
Jar "K" (Normal)	nitrogen duplicates,	Nos. 141, 142
Jar "L" (Anaerobic)	nitrogen duplicates,	Nos. 143, 144

The nitrogen content per 20 cc. of fluid in this set was as follows:

At the start of the experiment:

139—.00196	141—.00238	143—.00196
140—.00210	142—.00224	144—.00196

The day following:

139a—.00532	141a—.00588	143a—.00518
140a—.00532	142a—.00588	144a—.00518

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Two days from the start of the experiment:

139b—.00616	141b—.00658	143b—.00574
140b—.00616	142b—.00658	144b—.00588

Three days from the start.

139c—.00672	141c—.00715	143c—.00630
140c—.00686	142c—.00757	144c—.00616

Five days from the start:

139d—.01261	141d—.01079	143d—.00672
140d—.01275	142d—.01093	144d—.00686

Six days from the start:

139e—.01919	141e—.01765	143e—.00714
140e—.02031	142e—.01793	144e—.00729

Seven days from the start:

139f—.02031	141f—.03026	143f—.00743
140f—.02031	142f—.03054	144f—.00756

The following observations were made at the end of the experiment:

Jar "J" (Aerobic)—Fluid very turbid and milky in appearance; hide sank to bottom; hair removed with ease; hide was somewhat of a chalky white appearance with a faintly pinkish hue; fibers were somewhat gelatinized; the grain was badly affected but no holes were eaten through.

Jar "K" (Normal)—Fluid very turbid and milky in appearance; hide in normal suspension; hair removed with ease; hide was somewhat of a chalky white appearance though less so than above; fibers were slightly gelatinized; the grain was somewhat affected, but there were no holes eaten through the hide.

Jar "L" (Anaerobic)—Fluid only slightly turbid; hide in normal suspension; hair removed with ease; hide was of a bluish appearance and the fibers were in a well gelatinized condition; both grain and flesh side were in a perfect condition.

Set III of 400-gram hide pieces was as follows:

Jar "M" (Aerobic)	— nitrogen duplicates 145, 146
Jar "N" (Normal)	— nitrogen duplicates 147, 148
Jar "O" (Anaerobic)	— nitrogen duplicates 149, 150

The nitrogen content per 20 cc. of fluid in this set was as follows:

At the start of the experiment:

145—.00364	147—.00280	149—.00350
146—.00336	148—.00322	150—.00294

The next day:

145a—.00827	147a—.00855	149a—.00939
146a—.00841	148a—.00827	150a—.00953

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Two days from the start:

145b—.00925	147b—.00939	149b—.01191
146b—.00911	148b—.00929	150b—.01191

Three days from the start.

145c—.01023	147c—.00925	149c—.01317
146c—.01009	148c—.00939	150c—.01317

Five days from the start:

145d—.01653	147d—.01093	149d—.01485
146d—.01639	148d—.01068	150d—.01499

Six days from the start:

145e—.02340	147e—.01261	149e—.01653
146e—.02270	148e—.01261	150e—.01625

Seven days from the start:

145f—.02522	147f—.01723	149f—.01681
146f—.02536	148f—.01737	150f—.01667

The following observations were made at the end of the experiment:

Jar "M" (Aerobic)—Fluid very turbid; hair removed from hide with ease; hide whitish with a faint pinkish hue; fibers were somewhat gelatinized; grain was in a fairly good condition, although it had some yellowish discolorations in spots.

Jar "N" (Normal)—Fluid turbid; hair removed from hide with ease, general appearance of hide was white; fibers were very slightly gelatinized; grain badly deteriorated, but no holes were eaten through the hide.

Jar "O" (Anaerobic)—Fluid slightly turbid; hair removed with ease; general appearance of hide reddish blue; fibers were well gelatinized; grain and flesh sides were in perfect condition; cross section showed fibers to be of a decidedly bluish (gelatinized) color.

Discussion of Results

To facilitate interpretation of results, Tables I, II, III, and IV are given showing the total nitrogen in solution in each jar and the nitrogen by difference from the preceding giving the amount of nitrogen rendered soluble during the various intervals. The figures of the total nitrogen in solution indicate that the ratio of hide to the amount of water used is a factor which must be considered in selecting any of the soaking methods studied. Thus, when the ratio of hide to the water was 1 : 10 in terms of grams and cubic centimeters, the "Anaerobic" method caused the least amount of nitrogenous substance to go into solution at the end

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of both series of experiments. The "Normal" method caused the largest amount of nitrogenous substance to go into solution at the end of seven days' soaking in both series of experiments; however, at the end of ten days, the nitrogen in solution in the "Normal" method exceeded that of the "Aerobic." This seems to point to the importance of considering the duration of the period of soaking.

Where the ratio of the weight of hide to the volume of water was 2: 10, the "Anaerobic" method again caused the least amount of nitrogenous substance to go into solution; the "Normal" method stood the same as before at the end of the seventh day series. It is regretted that it was not studied in the ten day series and no indication as to the effect of time beyond seven days can be pointed out in this case. Where the ratio of the weight of hide to the volume of water was 4: 10, the amount of nitrogenous substance caused to go into solution at the end of seven days by each of the three methods tested were so close that they can be regarded as the same. However, at the end of ten days the nitrogen in solution in the "Aerobic" jar was the least, in the "Normal" jar the greatest, and in the "Anaerobic" jar considerably greater than in the first, but less than in the second. This again points to the importance of considering the duration of the soaking period in selecting any of the methods of hide soaking studied.

The figures of the nitrogen by difference from the preceding are of theoretical interest, and seem to point to the lack of regularity in the amount of nitrogenous substance going into solution during the time intervals of the soaking periods. In other words, the amount of nitrogen going into solution each day as the soaking progresses does not follow any regular curve.

The figures recorded under the bacteriological investigation are of interest, and are sufficiently striking to be self-explanatory. The observation of the condition of the hide pieces at the end of the second series of experiments brought out facts worthy of discussion. In all cases the hair removed with ease, indicating that prolonged soaking will enable to remove the hair from the hides completely. This is as it should be expected. The "Aerobic" method of soaking prevented gelatinization of the hide fibers, and caused a deterioration of the hide to a point of non-service-

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TABLE I.—Total Nitrogen Content in Jars of First Series of Experiments

Weight	Jar	Numbers	Condition	Control	One day	Three days	Five days	Seven days	Ten days
100 grams	A	151–2–3	Aerobic	0.05950	0.06907	0.09600	0.15981	0.23163	1.47973
	B	154–5–6	Normal	0.01150	0.04013	0.07300	0.32226	0.69616	0.95586
	C	157–8–9	Anaerobic	0.01850	0.06861	0.08916	0.11870	0.23621	0.56208
400 grams	D	160–1–2	Aerobic	0.06050	0.18113	0.28278	0.75939	3.03663	4.53188
	E	163–4–5	Normal	0.05350	0.21071	0.38016	1.90103	4.29884	6.46931
	F	166–7–8	Anaerobic	0.05850	0.22751	0.37195	1.09345	3.10658	5.64788

TABLE II.—Excess Nitrogen over Preceding Solution

100 grams	A	151–2–3	Aerobic	0.05950	0.00957	0.02693	0.06381	0.07182	1.24810
	B	154–5–6	Normal	0.01150	0.02863	0.03287	0.24926	0.37390	0.25970
	C	157–8–9	Anaerobic	0.01850	0.05011	0.02055	0.02954	0.11751	0.32587
400 grams	D	160–1–2	Aerobic	0.06050	0.12063	0.10165	0.47661	2.27724	1.49525
	E	163–4–5	Normal	0.05350	0.15721	0.16945	1.62097	2.39781	2.17047
	F	166–7–8	Anaerobic	0.05850	0.16901	0.14444	0.72150	2.01313	2.54130

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TABLE III.—Total Nitrogen Content in Jars of Second Series of Experiments

Weight	Jar	Numbers	Condition	Control	One day	Two days	Three days	Five days	Six days	Seven days
100 grams	G	133–4	Aerobic	0.02800	0.10206	0.12859	0.16611	0.28486	0.42389	0.54409
	H	135–6	Normal	0.03850	0.12327	0.15372	0.17773	0.52116	1.05639	1.66912
	I	137–8	Anaerobic	0.07350	0.17297	0.19390	0.21168	0.26474	0.30128	0.35595
200 grams	J	139–40	Aerobic	0.10150	0.26803	0.31535	0.35301	0.65430	1.02048	1.06823
	K	141–2	Normal	0.11550	0.29631	0.33719	0.38277	0.56513	0.92249	1.57078
	L	143–4	Anaerobic	0.09800	0.26096	0.29764	0.32445	0.35868	0.38697	0.40819
400 grams	M	145–6	Aerobic	0.17500	0.42050	0.47084	0.52902	0.85418	1.20014	1.23519
	N	147–8	Normal	0.15050	0.42351	0.47742	0.49374	0.57070	0.67151	0.91862
	O	149–50	Anaerobic	0.16100	0.47622	0.60818	0.68309	0.78476	0.87218	0.90607

TABLE IV.—Excess Nitrogen over Preceding Solution

100 grams	G	133–4	Aerobic	0.02800	0.07406	0.02653	0.03752	0.11875	0.13903	0.12120
	H	135–6	Normal	0.03850	0.08477	0.03045	0.02401	0.34343	0.53523	0.61273
	I	137–8	Anaerobic	0.07350	0.09947	0.02093	0.01778	0.05306	0.03654	0.05467
200 grams	J	139–40	Aerobic	0.10150	0.16653	0.04732	0.03766	0.30129	0.36618	0.04775
	K	141–2	Normal	0.11550	0.18081	0.04088	0.04558	0.18236	0.35736	0.64829
	L	143–4	Anaerobic	0.09800	0.16296	0.03668	0.02681	0.03423	0.02829	0.02122
400 grams	M	145–6	Aerobic	0.17500	0.24550	0.05034	0.05818	0.32506	0.34596	0.03505
	N	147–8	Normal	0.15050	0.27301	0.05391	0.01632	0.07696	0.10081	0.14712
	O	149–50	Anaerobic	0.16100	0.31522	0.23196	0.07491	0.10167	0.10742	0.03389

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ability. The "Normal" method of soaking caused the hide fibers to gelatinize some, resulting in considerably less of hide deterioration. The deterioration was sufficient, however, to make the hide completely unfit for tanning purposes. This was the case in both the 100- and 400-gram sets of the first series of experiments.

The "Anaerobic" method of soaking gelatinized the hide fibers to a high degree and so far as feel and appearance indicated, the hide suffered no deterioration. The following two phenomena when considered side by side tend to bring out a new point which may have practical bearing upon the present tendency to determine deterioration from the loss of hide substance as indicated by the amount of nitrogen in solution. The total amount of nitrogen in solution in the "Anaerobic" jar containing 400 grams of hide at the end of ten days was 5.6479 grams whereas in the "Aerobic" jar of the same set it was only 4.53188 grams or 1.11600 grams less. Yet, the condition of the hide from the "Anaerobic" jar was perfect, whereas the hide from the "Aerobic" jar had the appearance of one thoroughly decomposed. The question, therefore, arises—should not a method be sought which would enable the determination of the source and type of nitrogen in solution rather than its amount, in wishing to determine actual loss of hide substance?

Conclusions

1. Soaking and dehairing of hides can be accomplished in one step.

2. The "Anaerobic" method of soaking hides is very encouraging, indeed, a promising one for the accomplishment of the above.

3. The ratio of the weight of hide to the volume of water must not be too great in order that best results may be obtained. In the experiments described in this paper the ratio proved to be less than 4: 10 in terms of grams and cubic centimeters.

4. The duration of the soaking period is a factor of great importance. In the above experiments under "Anaerobic" conditions of soaking the period was less than ten days.

5. The number of bacteria per cc. was considerably less in the "Anaerobic" method than in any of the others.

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6. The amount of nitrogen in the soak solution may not be an indication of the extent of the loss of hide substance. The type and the source of the nitrogen should be determined before any conclusion is formed.

ADDENDUM

The writer offers his assistance with counsel or otherwise to any one wishing to continue this work. He will cheerfully assist in the practical carrying out on a small scale of his soaking method described in this paper.

WAUKESHA, WIS.

THE MODE OF OCCURRENCE OF TANNIN IN THE LIVING CELL*

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Whatever may be the decision arrived at by the chemists as to the chemical structure of the tannins, the microchemist—in the person of the botanist at least—must continue to speak of tannin in a collective sense. Even the distinction between "iron-blue" and "iron-green" tannin leads him but a very short distance in the direction of differentiating between various tannins in the living tissues, and, so far as we know at present, this distinction is of no significance from the physiological point of view. Since the botanist finds himself in this quandary, he is compelled to ask the indulgence of the chemist in permitting the use of "tannin" as a blanket term for a substance, or a group of substances, found in the living cell, having certain properties. These are (1) the power of coagulating proteins, the property which lies at the bottom of its ability to combine with hide to form leather, which is made use of in quantitative estimation of tannin in solution, and from which also is inferred its toxic action on the living substance, protoplasm, a highly complex nitrogen compound; (2) the readiness with which it is adsorbed by a variety of other organic substances, such as cellulose, a property which makes it of use as a mordant in dyeing; (3) its colloidal structure and the colloidal character of certain of its compounds with weak organic bases, notably the alkaloids; (4) its un-

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limited solubility in water and in alcohol, forming on drying a lacquer-like body, whose rate of solubility appears to be more rapid in water than in alcohol (Navassart, 1913); (5) its dialysability, the rate of which is higher in alcoholic solution than in water (Navassart, *l. c.*). Its greater dispersal in alcohol may be inferred from this. One may take for granted the usually recognized chemical reactions, but we should take note of the colloidal character of the compounds formed in many cases at any rate. It is this that Hillhouse (1887-8) many years ago apprehended when he insisted that the "form and appearance" of the "dark-brown gelatinous masses" formed in cells on the application of potassium bichromate rather than the colour of the

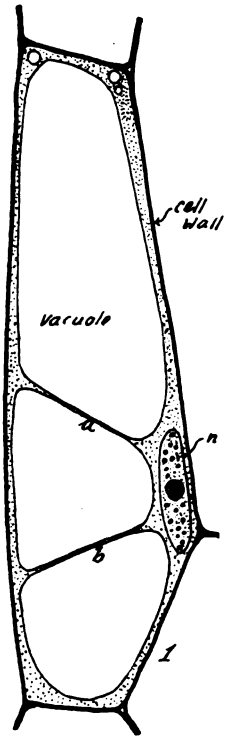

Fig. 1.—Generalized diagram of a plant cell, showing the cell wall, protoplasm with nucleus (n) and vacuole. The protoplasmic bridges marked *a* and *b* are threads and do not break the vacuole up into separate chambers.

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reaction were of importance for recognition, since other substances might reduce this reagent.

Setting aside these considerations for the moment, let us consider briefly the topography and some properties of the living plant cell. For our purpose we need regard only a relatively mature cell of a very generalized type. This consists of a sac of living protoplasm (the primordial utricle of early authors), in which lies embedded a nucleus. (Figure 1). The interior of the sac is filled with sap containing solutes which occur in concentrations usually equivalent osmotically to a 0.3 to 0.4 N potassium nitrate solution, though this may vary between 0.1 N (in the egg-apparatus of *Torenia,* Lloyd, 1916) and a concentration having about thirty atmospheres osmotic pressure (Harris, Lawrence and Gortner, 1916). It is obvious that if such is the case, and in view of the fact that protoplasm is semipermeable and a semi-fluid of considerable viscosity, the protoplasmic sac, when placed in water would become distended, or, otherwise expressed, would

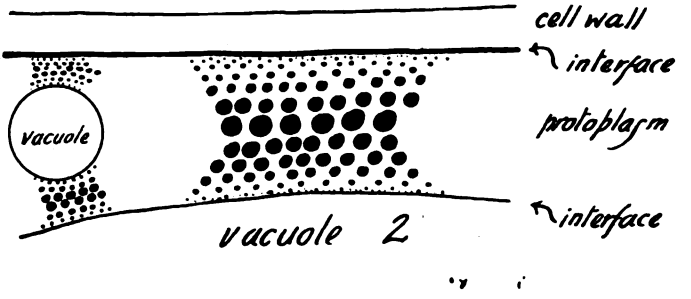

Fig. 2.—A diagram in simple terms to illustrate the structure of protoplasm.

undergo turgescence which would approach an equilibrium determined by the distensibility and strength of the membrane. This equilibrium is however not usually reached because of the presence of a cellulose cell wall, itself somewhat distensible when wet, and this membrane imposes a sharper limit on the turgescence, since the protoplasmic membrane lying against the cell-wall is supported by it, just as the rubber ball is supported by the leather of a foot-ball. I have been able, under special condition, to observe the escape of the entire protoplast undamaged

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out of the supporting cell wall (Figure 3), so that it lay free in water, where it assumed an almost perfectly spherical form, its departure therefrom being due to the presence of bodies of different viscosity than that of the protoplasm proper (*e. g.*, the nucleus). The total volume of the isolated cell must have been

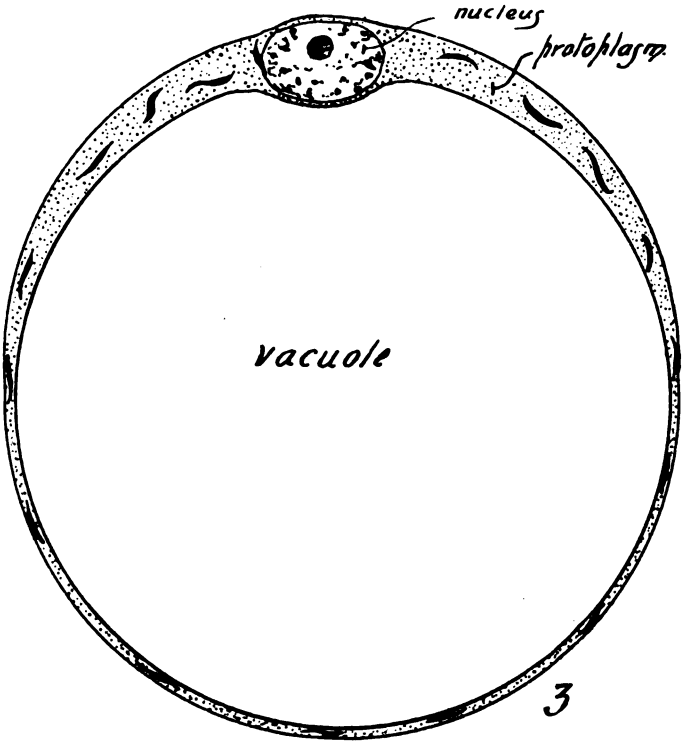

Fig. 3.—A plant protoplast which has escaped from a ruptured cell wall, and lying free in water. (From the Japanese persimmon, *Diospyros kaki*). The spindle shaped bodies in the protoplasm are carotin bodies. Semi-diagramatic.

greater than when imprisoned within the cell wall. (Note 1). It is obvious that if a hypertonic solution is placed in contact with a living cell, the protoplast must contract (plasmolysis) and it may then result that substances in solution before this contraction sets in, are, by increase in concentration, thrown out of solution.

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The semipermeability of protoplasm, though not a fixed property in a quantitive sense, but one which varies with changing conditions within certain limits so long as life is maintained, appears to be a peculiarity chiefly if not wholly of the limiting membrane, either on the outer surface or on that lining the vacuoles or both. It is to Pfeffer and de Vries that we owe our fundamental knowledge of this membrane, which however is the object of much research at the present time. Without digressing on this theme, it must be pointed out that this membrane is a part of the living protoplasm, though it must be said also that in it there will be concentrated at its surface, such substances (*e. g.*, lipoid, Overton) as would do so in a system composed of colloids, etc., of different surface tensions. Nevertheless, we must believe at the present that the living substance constitutes the outer phase of the system, understanding of course that itself is a protoplasm-water system of which protoplasm-rich water is the outer phase (Figure 2).

It will be obvious that, in the absence of some special mechanism, water-soluble substances must come into contact with the limiting membrane, and, if the dimensional relations permit, must diffuse into it. Thus, some dyes, for example the so-called intravitam stains (methylene blue, neutral red, etc.), can diffuse through the protoplasm, others cannot except when death intervenes (eosin, etc.). Even salts of small molecular size, or their ions, even those to which protoplasm is semipermeable, diffuse more or less, and cause, at suitable concentrations, sufficient alteration in its physical condition to increase or to decrease its permeability. It is not less obvious that substances which are toxic to protoplasm and which are water-soluble when brought into contact with the limiting membrane must attack its surface at least even if these substances are such toward which the protoplasm is semipermeable. When however it is permeable, as it is toward the alcohols, ether, etc., these pass through without measurable hindrance so that their toxic effect may come into play throughout the whole protoplasmic mass.

Distribution of Tannin in Plant Tissues, and in the Cell

This brings us to the question of the position in which tannin occurs in the cell and in tissues. It was formerly believed that it was to be found in the nucleus, in starch grains, cell-wall, etc.

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(Dekker, 1913), but this proved to be in error. These appearances are always to be explained by the escape of the tannin into these bodies on the death of the cell. The tissues of the bark of tannin-bearing trees invariably shows a pronounced tannin-reaction in the cell walls of the parenchyma[1] after drying, after preservation in alcohol, or after soaking in water. When properly treated with potassium bichromate as Sanio long ago found, or vapour of nitrous ether, however, the strict confinement in the interior of the cell is made clear. (as, *e. g.*, in the banana, Figure 9). Furthermore it has been abundantly proved also that the tannin occurs in solution in the vacuole, or vacuoles, and not in the protoplasm, or any part of it. (af Klercker, 1888, van Wisselingh, 1910, 1914).

As to its distribution in tissues, tannin has been found in both embryonic, definitive and completely static tissues. Its occurrence in growing and reproducing cells of the alga *Spirogyra* and other similar forms has long been known (Pfeffer, 1886, de Vries, 1885, etc.). It has been found in the embryo-sac (Phoenix, Lloyd, 1910), in the developing endosperm, and in other growing tissues, from which in some instances it later disappears (endosperm of Phoenix, Lloyd, *l. c.*), from others not, as in the tanbark oak (Mell, 1911). On the other hand, it is commonly found in definitive tissues such as the medullary ray cells, cortical cells, pericycle and epidermis of *Eriogonum nudum* (Note 3) in which it seems in all cases to remain permanently, or to be changed more or less into condensation products (Drabble and Nierenstein, 1907) as in the formation of cork (Note 4). In tissues which are completely static—that is, which have run their course and undergo no further development or any change but that of disintegration, tannin is very frequently met with. The dead or moribund tissues of the cortex (cork, etc.) should here be included, as also the enclosing tissues of the walls of fruits (endo-, meso- and ectocarp), the coverings of seeds, and the heart wood of many trees. Without entering into too great detail, it may be summed up by saying that tannin of some sort or other is to be met with in every possible kind of tissue and during every possible stage of development (see Dekker, 1913).

[1] The stone cells do not show it in the California tanbark oak.

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It must be evident that in such various positions and relations the tannin can hardly be the same substance chemically, especially if it can be shown that the tannin serves different functions in the metabolism of the plant. This question has long been a matter of debate, and it is not part of our purpose in this paper to consider the evidence on this point. I may merely state that now the evidence is fairly conclusive that tannin, in some situations, enters into the carbohydrate chain, leading up, *e. g.*, to the growth of the cell-wall in the alga *Spirogyra,* according to van Wisselingh (1910). Also I have shown that its occurrence in the developing seed of the date is such as to admit of scarcely any doubt that it plays a rôle in the metabolism of the developing endosperm and embryo.

De Dominicis (1919) has recorded observations on the European chestnut which indicate seasonal changes in the tannin content of the cortex, which he regards as pointing to a metabolic function chiefly resting upon its easy oxidation. He cites in support of his interpretation the view that tannin disappears from fleshy fruits through complete oxidation (Gerber, 1896). I have, however, already shown that this is not the case, and that as a matter of fact oxidation of the tannin in fleshy fruits sets in after non-astringency has been accomplished and after death of the cells has intervened.

Mode of Occurrence of Tannin

It is equally evident, if the foregoing statement as to its functions in the plant be true, that its mode of occurrence can hardly be the same. This brings us presently to consider the possibilities involved, so far as we are in a position at the moment to consider them. In order to do this without loss of effort, I shall ask your consideration of concrete cases, typical of general conditions.

(1) The case of *Spirogyra.* This plant is the common "water-silk" or, more poetically "mermaids' tresses." Most careful physiological studies of the behaviour of the tannin content of this plant have been made by van Wisselingh (*l. c.*), and it is to these we owe chiefly our present understanding of the conditions here obtaining.

According to him, the tannin in *Spirogyra* (Figure 4) occurs in simple solution in the cell-sap in the vacuole. This tannin

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he regards as essentially the same as gallnut tannin. The evidence is so extensive and complete that we may regard it as sufficiently convincing for our purpose. When the cell is killed, the tannin

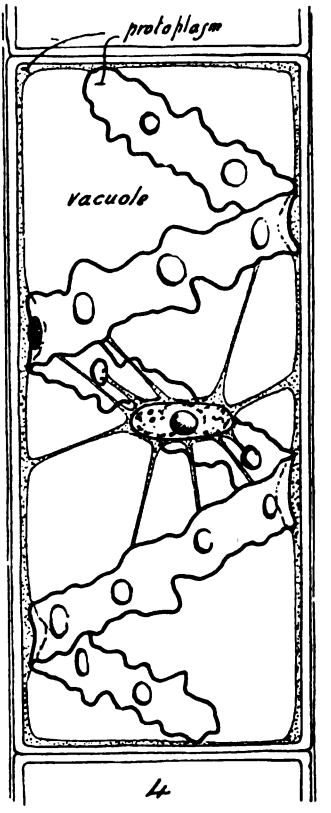

Fig. 4.—A cell of *Spirogyra*. The spiral band is the chloroplast; otherwise the structure is as in Fig. 1.

diffuses into the protoplasm and its presence there can be demonstrated by reagents, (Note 5). What then keeps it in the sap during life? Tannin combines with proteins with great ease, and it is easy to infer that the tannin in the sap would therefore attack the limiting protoplasmic membrane. That it actually does this is a view which has been supported by af Klercker (1888), following earlier workers, who has argued that, as in the artificial gelatine-tannate cells studied by Traube and himself, the precipitation membrane so formed hinders the further penetration of

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the tannin into the surrounding protoplasm. Interesting as this view is, it must, I think, be admitted that the evidence which af Klercker depended on is not convincing.

Another view of the matter is that the tannin is combined in some manner with another body dispersed or dissolved in the cell-sap. I shall show shortly that this condition certainly exists in many other tannin cells. That it occurs in *Spirogyra* is doubtful, though Pfeffer (1887) held that albumin is present, but that the presence of organic acid prevents precipitation. Van Wisselingh on the other hand has denied the verity of Pfeffer's views, as also those of Loew (1906) and Bokorny, who hold that "active albumin" is present.

(2) The case of tannin idioplasts in certain fleshy fruits and elsewhere. I turn to the other extreme of my series of instances, for the reason that the condition presented by these tannin cells is probably the best understood of all. (Note 7). In these, the tannin is clearly associated with a second substance, by which it is adsorbed. This substance was identified by Ernest F. Clark (1913), as a carbohydrate.

The fruits of the persimmon in their unripe condition are strongly astringent. Those of us who have lived in the persimmon belt well know the pucker produced on eating this fruit when not fully ripe. The Japanese long ago learned how to reduce this astringency in their cultivated varieties at an increased rate, so that the fruit, when treated by them (Note 6) becomes edible while still firm, which otherwise would not be the case.

If a bit of the soft or watery tissues from a very ripe persimmon or banana is shaken up in water, the cells will fall apart. Certain of these, on standing, will settle rapidly to the bottom of the vessel. On microscopical examination, these can be seen to be composed of a cell wall lined with a delicate layer of protoplasm, enclosing a more or less irregular colourless glassy mass (tannin-mass) which can be cracked and crushed like a piece of firm gelatine (Figures 5-8). They are really hard enough to make the fruit feel gritty to the teeth when eaten. On exposure to the air (oxygen) they turn dark red-brown. Tannin reagents which produce colour reactions will cause them to become coloured, but there will be no precipitation. Alkaloids, for example, causes a small amount of shrinkage and a very slight

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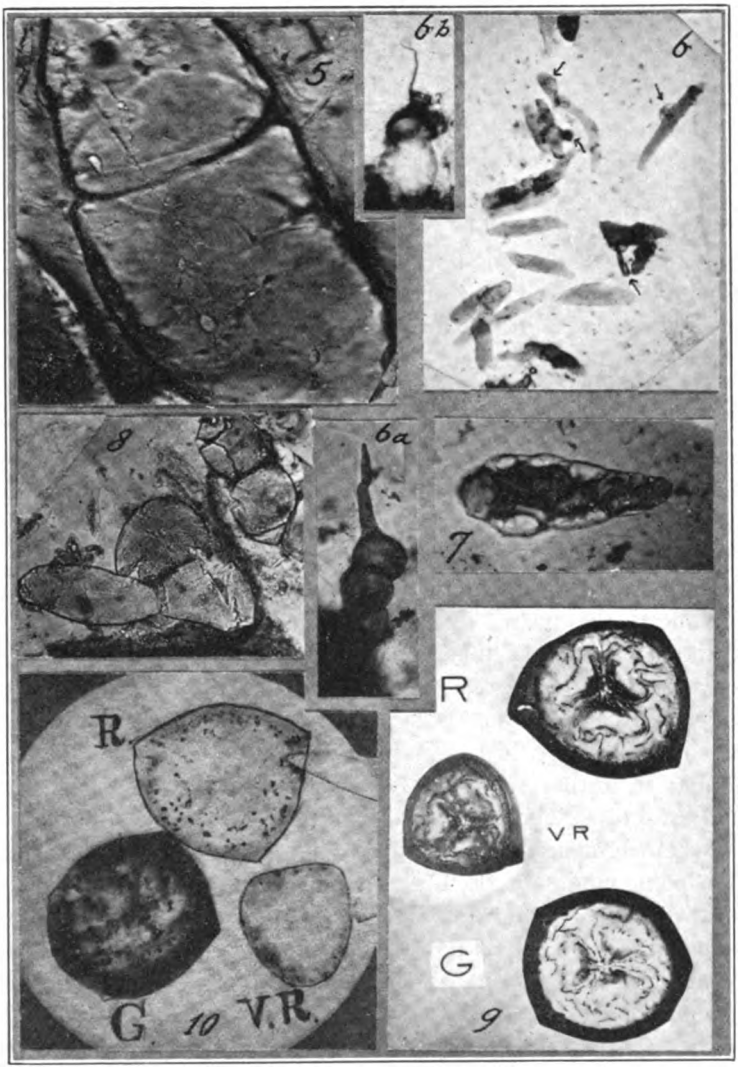

Fig. 5.—Tannin mass isolated from the ripe pericarp of the Japanese persimmon (*Diospyros kaki*). The internal structure, consisting of canals and fusiform or spherical cavities, is clearly shown. This gelatinous mass is the carbohydrate substance which adsorbs the tannin.

Fig. 6.—A number of isolated tannin masses on a smaller scale of magnification. The arrow points indicate precipitation membranes. Two such may be seen at higher magnification in Figures 6a and 6b.

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Fig. 7.—A single tannin mass after standing three years in water. Syneresis has taken place.

Fig. 8.—Tannin masses from the pulp of a ripe banana, in which fractures produced by pressure can be seen.

Fig. 9.—Transverse sections of green, ripe, and very ripe banana, showing the distribution of the tannin cells after exposure to nitrous ether.

Fig. 10.—Adsorption prints on filter paper from the same.

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yellowing, but no visible granulation (Note 9). On standing in water or alcohol, tannin can be extracted, but not completely. I have kept these tannin masses, as I have called them, for ten years in water, and they are still intact and show appropriate reactions. Many of them have undergone internal shrinkage (syneresis) as seen in Figure 7. When fresh tannin masses are placed in water the diffusing tannin may be sufficient to form precipitation membranes with the associated colloidal substances invariably present (pectose, etc.), and these are likewise preserved indefinitely (Figures 6, 6a, 6b). The tannin content may however be completely destroyed by boiling the tannin masses in concentrated nitric acid for a very short time. If the boiling is prolonged, the masses swell up and disintegrate. When stopped at the right moment, the masses remain in the original form, but now show no tannin reaction. Analysis of this substance proves it to be a carbohydrate (Clark, 1913). The tannin-mass which we have just considered is therefore a colloidal complex very similar to leather, save that the adsorbing substance is a carbohydrate rather than a protein. I purposely avoid the question as to whether finally we have to do with a chemical or an adsorption compound, nor do I pretend to discuss what is meant by adsorption. The term serves its purpose here without going behind the term. It is however of interest in this connection to recall that the amount of astringency of a fruit such as persimmon or banana can be estimated closely by making use of the partition of adsorbed tannin between the tannin masses and another convenient adsorbing substance, such as filter paper (cellulose). If a green, ripe and very ripe banana are cut, and filter paper is placed in direct contact with the cut surfaces, adsorption prints are obtained, which, on development with a suitable reagent, show adsorbed tannin in inverse amounts to the degree of ripeness (Lloyd, 1916a), (Figures 9, 10). When the

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fruit is examined before the onset of astringency, the tannin-masses are found to be soft and yielding, the more so the more immature the fruit. Correspondingly the more readily the tannin escapes until, when examined early enough, the two substances, tannin and its associated colloid (emulsoid), flow out together as a fluid, which however may be coagulated by appropriate means. We may therefore conclude that, in such instances as we have just regarded, the tannin is associated in the cell sap with a second substance, a carbohydrate emulsoid, by which it is adsorbed. It is significant that the tannin is never found in the protoplasm or cell wall of the living cell. Even when, as may happen when the unripe fruit is bruised (Lloyd, 1916), the tannin-masses burst forth from the cells and flow into the intercellular spaces, the tannin is held from spreading. There is evidently an equilibrium of a remarkable nature here.

The emulsoidal nature of the associated carbohydrate can be very clearly seen in tannin masses which are yet not quite passed into the definitive condition. When such are placed in dilute alkalies or acids, they swell enormously, showing clearly their gel structure. This is to be seen also in the unaltered structure of the mature tannin masses, which are penetrated by canals extending from spindle-shaped or spherical cavities (Figure 5), the origin of which I have elsewhere attempted to explain. (Lloyd, 1922).

We have now seen that tannin may occur within the living cell in simple solution or, again, associated with another substance of colloidal nature, by which the tannin is held firmly by adsorption.

In the light of these examples, I wish now to consider the condition which the members of this association will be more directly interested, namely, the mode of occurrence of tannin in the tanbarks. I will consider here the California tanbark oak. The distribution of tannin cells in this species has been described by Mell (1911).

The tannin, it will be seen from the illustration, (Figure 11), is to be found in the parenchyma everywhere, including the thick-walled cells called stone cells. When dried material is examined after soaking in alcohol (95 per cent) these cells are found to be collapsed and devoid of tannin. All the cell walls however,

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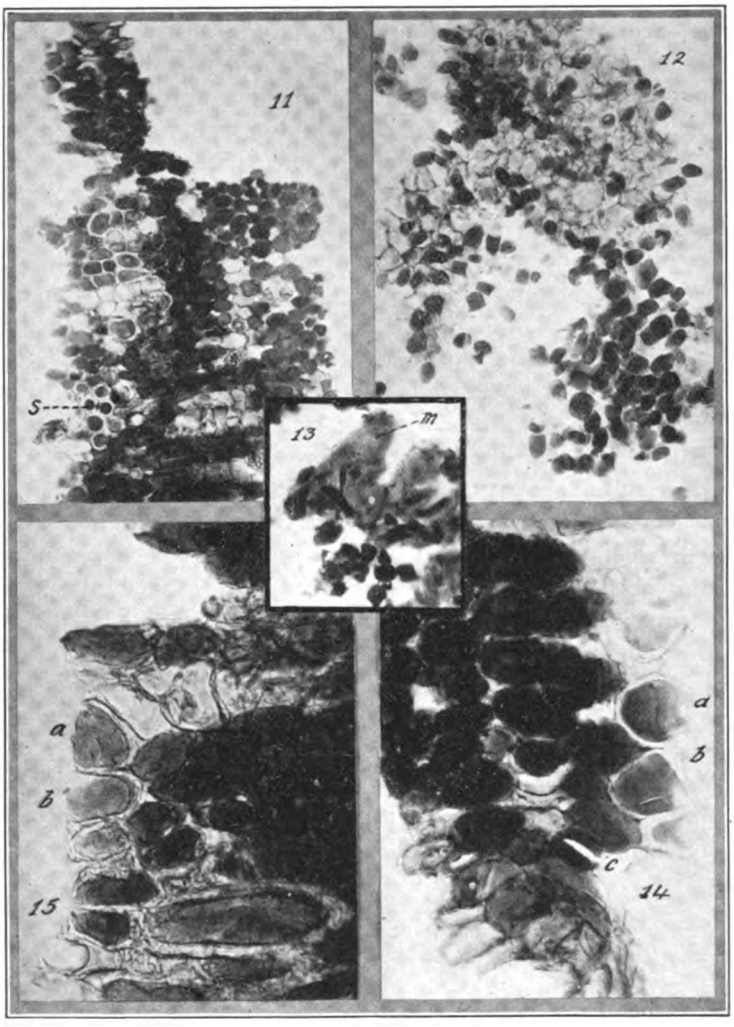

Fig. 11.—Section of the tannin-bearing tissue from the secondary cortex (bark) of the California tanbark oak, after preservation in alcohol. The parenchyma cells are seen to be filled with a cheesy substance, insoluble in water. *S.*, stone cells.

Fig. 12.—A similar section after treatment with concentrated sulphuric acid. The cell walls are, for the most part, totally destroyed, setting free the tannin masses. A part of the tissue, however, still remains recognizable as such.

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Fig. 13.—From a preparation still further acted upon by concentrated sulphuric acid, so that the stone cells have been reduced to a mucilaginous mass (*m*) in which lie embedded some still unaltered tannin masses.

Fig. 14.—A small portion of the section reproduced in Fig. 11 (extreme upper lefthand of that section). In this the tannin masses can be seen to have been cracked (*b*, *c*), and scratched in parallel lines by the edge of the razor (*a*). Indication, also, of the protoplasm and nuclei can be seen in some of the cells.

Fig. 15.—The thin edge of a section of material preserved in alcohol and treated with fairly strong ammonia. At *a* and *b* especially the tannin masses have preserved their thin edges, showing clearly their resistance to this reagent. The details of the photograph indicate that the gel is not as firm as that in Fig. 14.

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excepting curiously enough those of the stone cells, show a pronounced tannin reaction. As would be expected, this does not give us any real idea of the mode of occurrence of the tannin in the living cells. The more usual method for this purpose is that used by Mell as explained in his account just cited, and first used by Sanio (1863)—namely, fixation with potassium bichromate. My own experience shows that this reagent does all that is expected of it. Tissues thus treated or, also, after exposure to vapour of nitrous ether (Vinson, 1907) usually show cells completely or partially filled with dark brown transparent glassy masses, especially when the cells are rich in tannin. If the amount is small, granulations of the same general character occur. If flakes of commercial gallnut tannin are exposed directly to the action of strong potassium bichromate, clear glassy masses of brown colour are also formed which superficially at least appear to be identical in composition with the "amorphous tannin" of af Klercker (1888), (Note 8) formed in cells with the same reagent. Ferric chloride produces the same colour reaction as on unaltered tannin.

If on the other hand samples of the fresh tissues are placed directly in alcohol (Note 9) this of course extracts tannin, as is shown by testing the extract. If however thin sections are examined microscopically in water, all the tannin bearing cells are found to be completely filled with a glassy substance which breaks and otherwise behaves just as fragments of a dense gel. (Figures 11, 14, 15). It shows parallel lines or scratches caused by the cutting edge of the razor, fractures of various sorts, some-

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times starch grains, small inclusions similar to those seen in the tannin masses from persimmon, etc., and has evidently a cheesy consistency. These masses show tannin reactions as to colour only however. Lead acetate leaves them homogeneous (Note 10).

In weak ammonia for 24 hours, they show no change save a red colouration. The minutest details of fracture of the glassy cell contents are preserved (Figure 15). Nor are they attacked, at least within some hours by sodium hydrate, or ammonia copper hydrate, and they are equally resistant to the acids. Sulphuric acid (conc.) hydrolyses the cell wall around them without attacking themselves (Figures 12, 13). Nitric acid is equally ineffectual, though they do not show a tannin reaction afterwards. They may be stained equally by methylene blue both before and after treatment with nitric acid, showing that the methylene blue staining of these bodies is not due to the presence of tannin (Note 11).

In Schultz's macerating agent HNO_3 and potassium chlorate) the tannin masses become softer and finally are completely hydrolysed though they are nearly as resistant as the secondary cell walls. Figure 16 shows two cells separated by maceration (for 2 hours) in which the protoplasm and nucleus are visible,

Fig. 16.—Two cells after about one hour in Schultz's macerating reagent, and crushed. The cell wall and the gelatinous tannin mass both show the resulting cracking.

and the gelatinous contents of the vacuole broken and cracked by pressure, the cell walls also being cracked open. After 6 hours' maceration in the cold the tannin masses may no longer be cracked and fragmented, showing that hydrolysis has progressed.

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After standing 12 hours in glycerine the hydrolysis becomes completed, and the masses are no longer to be found, which does not occur after one hour's treatment with the macerating reagent.

It may therefore be safely concluded that the substance which occupies the vacuole of the tannin cell in the tannin bearing tissues in the tanbark oak is a colloidal complex of tannin and an emulsoid. The chemical nature of this latter is not clear. It shows no cellulose or starch reaction, remaining yellow after exposure to hydrolysing agents on testing with iodine.

It seems therefore to be rather more closely related to the mucilages. Aside from this its physical similarity to the tannin masses of the persimmon and banana, etc., is evident, and the association with tannin appears of quite similar nature.

It will be seen that the tannin masses in the California tanbark oak occupy an intermediate position between those of fleshy fruits and the conditions which we assume to be true of *Spirogyra*, in that, while evidently composed of tannin and a second emulsoidal substance, they show different solubilities and hydrolysis relations. It is, I think, evident that the condition is comparable to that frequently met with in other plants—certainly, for example, to that in *Eriogonum* and in the acorn of *Quercus laurifolia* (Lloyd, 1912). The "amorphous tannin" seen in many instances by af Klercker, the alcohol insoluble tannin seen by Trecul (1865) and by Baccarini (1893) in the Leguminosae, and more recently in certain plants of this family by Miss Staber (1903) and Miss Goodale (1909) are other examples of an analagous if not identical condition. I have recently also examined the bark of the chestnut oak and of the Western hemlock, and find evidences of this same condition; but I hesitate to make any detailed pronouncement at this moment, inasmuch as I have had no access to living material. As I have already said, the cortical cells upon death give up their tannin by diffusion to the surrounding cell walls and other adsorbing substances in the neighbourhood. The application of any tannin reagent, therefore, can give us no information about the original mode of occurrence. After escape from the living cell, chemical changes of some order always take place, giving rise to a doubtless considerable variety of colouring matters; some of which are quite readily extractable in alcohol, as for example, the purplish-

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red colouring matter in the cork cells of the Western hemlock; while others are more extractable in water. It is, therefore, perhaps quite proper to speak of the tannin-infiltrated tissues in the bark as a sort of vegetable leather; and, if we may venture to speculate in teleology, the bark is thus rendered more efficiently protective to the living tissues of the tree than it would otherwise be.

Reasonable limitations to this paper will not permit me to go into further detail. I may, therefore, sum up the foregoing account as follows. According to our present knowledge, tannin, in the living cell, may occur as a solution in the cell sap. It is safe to assume that other substances, including salts, sugars, etc., some or all, are always present. There is evidence that certain of these may be able to link up with tannin in some way so as to prevent its attack upon the living protoplasm. The view, however, that this is accompanied by the formation of a precipitation membrane with the protoplasm itself is not well founded. It would be interesting in this connection to know what the relation of the alkaloids to the tannins may be in such forms as the coffee and tea plants. The tannin which occurs in this way seems to be plastic—that is, to be useful in the metabolism of the plant. On the other hand, it is now certainly known that in many cases a second substance, capable of adsorbing the tannin, is present, and that this adsorption relation becomes more complete with the maturing of the cell. This second body is, in some cases, such as fleshy astringent fruits at any rate, a carbohydrate; in other cases it has similar physical properties but differs apparently in the fact that with the death of the cell the tannin escapes. This is probably due to the fact that in many situations the associated adsorbing body is itself water-soluble—as appears to be the case in the tanbark oak. While the cell is still living, however, its function is probably the same as in the case of the fleshy fruits. The subject, obviously, is one which will permit of much further investigation.

Notes

Note 1. When the parenchyma of the mesocarp of the fruit of a completely ripened Japanese persimmon (Diospyros Kaki) is teased out in water, the cell walls, which have been partly

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digested, and thus much weakened or even perforated, sometimes rupture and the protoplasts migrate into the surrounding medium. Most beautiful examples of free, naked protoplasts in the living condition may thus be obtained.

Note 2. Eriogonum nudum. The cells of the pericycle and epidermis of the developing long internodes during development contain much tannin which is associated with a caseous mass which entirely fills the vacuole. This cannot wholly retain its tannin in alcohol, but itself remains in undiminished volume. It is insoluble in water or in weak ammonia.

Note 3. This is beautifully seen in the phelloderm of the Western hemlock, which is recognizable as purple curved streaks in the bark. If a dried piece of bark is placed in alcohol some of the coloring matter is quickly dissolved out. Sections show under the microscope cork cells filled with alcoholic solution of the same, which apparently does not readily diffuse out through the cork cell walls.

Note 4. The presence of tannin in solution in the sap of *Spirogyra* may be demonstrated by means of the alkaloids (weak bases) which penetrate the protoplasm easily and form a colloidal precipitate in the sap. Overton, Czapek, et. al. see van Wisselings, *l. c.*

Note 5. The tannin idioplasts referred to occur in the fruits of the date, (Thornber, Vinson, Lloyd) Persimmon (Tichomirow, Lloyd) St. John's bread, *Ceratonia siliqua* (Flueckiger Tichomirow), *Achras* and *Musa,* Banana (Lloyd, 1911), etc., see Lloyd, 1911, 1922.

Note 6. The Japanese enclose unripe persimmons in saké barrels, wherein which the fumes of alcohol, it may be, hasten respiration and thus cause the accumulation of carbon dioxide. Following this lead I have been able to treat persimmons (Japanese varieties) with carbon dioxide at different pressures and to induce non-astringency at corresponding rates, up to certain limits.

Note 7. Phloroglucin is also present. Tichomirow (1905) called the substance a phloroglucotannoid.

Note 8. Appearance of the kind led af Klercker to say that "tannin occurs in plant cells in two forms, as a solution and as solid (nichtfluessige) amorphous masses or balls, of which the

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first is by far the most frequent. Where the substance occurs as solution, it does so in two ways, as already Naegeli and Schwendener have pointed out: the tannin is in solution along with other substances to form a single cell sap, or it is separated from them and then takes on the form of a viscous oil-like masses ('Gerbstoffblasen'), (*l. c.*, p. 17). I have not been able to see eye to eye with af Klercker in this matter, for, as I say elsewhere in this present paper other substances can, when coagulated, contribute to give the optical appearances which may have led him to the conclusions stated."

Note 9. Samples of California tanbark oak were placed in alcohol in 1918. This material, collected near Carmel, California, has been examined by me from time to time. The illustrations were made from preparations of this.

Note 10. Physical behaviours of dry gallnut tannin when acted on by various tannin reagents, especially in strong solutions are frequently surprising and most unexpected. When flakes of tannin, or a very concentrated solution, are placed in strong lead acetate no ppt. is produced. Instead, a homogeneous pptn. membrane is formed on the surface of the flake, or resp. solution, preventing the entrance of the reagent, but permitting entrance of water. "Growing" pptn. membranes also occur. On the addition of ferric chloride, the strong solution of tannin inclosed in the flake swells, and the membranes become crinkled. Blue reaction intervenes. On adding tannin flakes to concentrated sulphuric acid, they become minutely fissured by the sudden extraction of water. On adding water, the acid at once attacks, the flakes dissolving with a red colour reaction (oxidation). Merely the absence of internal ppt. in the tannin masses alone is therefore insufficient as optical evidence, but must be supported by other evidence.

Note 11. Van Wisselingh holds that methylene blue does not react with tannin.

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COMPARATIVE OBSERVATIONS OF THE TANNING PROPERTIES OF VEGETABLE TANNING MATERIALS, SYNTHETIC TANS, AND MIXTURES OF VEGETABLE TANNING MATERIALS WITH SYNTHETIC TANS *

By S. Kohn, J. Breedis and E. Crede.

Introduction

The complex nature of the tanning process makes the evaluation of tanning materials by analytical methods very difficult. A number of articles were published recently on the merits and shortcomings of the official hide powder method, and although these papers were almost entirely confined to vegetable extracts, the new viewpoints gained are really of greater importance for the investigation of syntans. As far as the vegetable extracts are concerned, it would seem that the relative value of the different types of extracts is so well established that the introduction of new and more involved analytical determinations cannot possibly change matters materially, because it cannot possibly amount to anything but a conventional agreement to accept such measurements as a criterion of the actual tanning value in the tannery, which latter

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however, is too complex to be measured directly and adequately by laboratory methods. This fact has been recognized for so long a time that it has become sub-conscious with most of us but all our dealings with vegetable extracts reflect and imply this recognition.

Sooner or later the syntans will be in a similar position. Their practical value in tanning, filling, bleaching, swelling, dispersing power, equalizing of penetration, acceleration of tanning process, etc., constitutes a sum of influences so complex that we cannot possibly think of devising a method of analysis which would do justice to all of these functions. But as in the case of vegetable tans, the sum of all functions will nevertheless impress itself so strongly upon the mind of the practical tanner, by the visible and tangible results on the leather produced, that he will buy syntans, as he buys gambier and quebracho, for their intrinsic value, and use some conventional method of analysis as a means of ascertaining the degree of concentration.

Before this time arrives, however, that is before the syntans have worked themselves into a place of standardized application and appreciation, and in order to help bring about this final development, it behooves us to use every accessible scientific measurements to demonstrate the properties of these relatively new products. We have therefore shown in a previous paper[1] how comparative observations on the quality of syntans of different composition can be carried out by using as a criterion the degree of independence from the concentration and have also shown how the correct acidity of syntans can be determined. In the present paper we shall study the characteristics of a certain type of synthetic tans by comparing their properties with those of vegetable extracts. We shall confine ourselves here to laboratory methods, which of course are not meant to replace, but to supplement and explain the results achieved in the tan yard.

Comparative Tanning Experiments: In these experiments we used hide powder but our procedure differs in several respects from the practice used in the official method and the Wilson-Kern method. For a closer approach to tan yard conditions, we use solutions of higher than analytical concentrations, extend the period of tanning over several days and use an excess of tanning

[1] *J. A. L. C. A.*, 17, 4, p. 166.

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TABLE I.—QUANTITIES IN MILLIGRAMS REMOVED BY 100 cc. WATER IN THE CONSECUTIVE WASHES.

Tanning material	Washings: 1st	2nd	3rd	4th	S(1 to 4)x2	5th	6th	7th	8th	9th	10th a[1]	10th b[2]	11th	12th	13th a[3]	13th b[4]	14th	15th	16th	17th	18th	19th	20th	Tans of second order S (5 to 20) x2	Weight of tans resisting 20 washes	Weight of air dry tanned hide powder gms.	Per cent protein	Per cent water	Per cent of tannage based on protein
Corbanol	688	243	114	52	2194	43	32	29	25	24	19	22	27	18	15	19	15	13	11	10	13	10	10	709	2025	22	72.4	14.26	17.8
Mixture of quebracho and Sorbanol (x)	532	193	124	80	1957	82	64	74	61	61	53	60	72	40	42	46	38	35	33	32	31	29	29	1764	10200	30	51.2	14.33	66.5
O. S. M. quebracho	1044	361	219	152	3551	126	115	107	95	91	80	96	105	59	60	66	55	50	43	47	44	40	37	2630	8745	30	54.6	15.75	53.4
Tannic acid	547	266	223	183	2436	141	175	155	205	165	218	290	214	176	128	147	102	108	76	119	77	55	43	5188	9450	30	53.2	14.8	59.3

Remarks: [1] Shaken for 30 minutes.
[2] Shaken for 1 hr. 30 min.
[3] Shaken for 1 hr.
[4] Shaken for 2 hrs.
All washings up to 10 were done by shaking for 30 min.
All washings from 15 on, for one hour.
(x) Prepared under definite conditions as to temperature, proportions, etc.

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material. Then we observe how this perfectly tanned hide powder behaves toward washing and determine not only the amount of active constituents retained in the "leather" after exhaustive washing, but also the amounts after any chosen number of washings.

This will be best understood by referring to the figures in Table I. For all experiments we used 20 grams of air dry hide powder to 1 liter water containing 5 grams of active ingredients. After 24 hours, tanning material corresponding to 10 grams of tannin was added, after another lapse of 24 hours 20 grams, so that a total of 35 grams of actual tan was used on 20 grams hide powder. In some experiments we increased the concentration up to the limit used in the extract wheel.

The tanned hide powder was liberated from excess of tan solution by squeezing through filter cloth and was washed twenty times with 200 cc. distilled water, shaking one-half to two hours for each wash. About one-half of the clear filtrate of each washing, amounting to 100 cc. was evaporated, weighed, tested for nitrogen, and the hide powder itself after the twentieth wash was analyzed for hide substance, ash, fat, water and tan.

Before we enter into a discussion of the data in the first table, we shall point out shortly a set of definitions which we have introduced and used in our laboratory for some time to good advantage. Like everybody else we have been laboring under the drawback that in the intercourse between the members of our chemical staff, the term "tan" was used in a very vague way, meaning in one case this, and in another case something different. Analyzing this difficulty, we gained the impression that the root of the evil lies in the fact that the usual definition of "tan" attempts to combine two items which should be kept apart if confusion is to be avoided. The property of changing hide into leather is one thing and the resistance to washing another thing entirely.

We found that although in some instances, we have made good use of the distinction between combination tans and adsorption tans, in the majority of cases we are better off if we abstain from any more or less hypothetical assumption about the tanning process being due to chemical combination or to absorption. We therefore divide the active ingredients of tanning materials into

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tans proper and co-tans. The first group comprises all bodies which are capable of transforming hide into the imputrescible and pliable substance called leather. The second group comprises all bodies which cannot change hide into leather but which have nevertheless the property of being taken up and retained by hide substance and play a certain rôle, not well defined as yet, in the process of making leather. The tans proper as well as the co-tans are then to be sub-divided into two, three or more orders or classes, depending upon the degree of permanency of the combination resulting from their action upon hide substance. Where we draw the line between tans of the first order and tans of the second order is open for mutual agreement.

We turn now to the figures in the table. We have assumed that four washes on finely divided hide powder under the conditions described will remove all excess tans and inert matter, which were hanging on mechanically and also tans proper and co-tans of the first order, or of the lowest degree of permanency. We further found it expedient to call all bodies resisting more than four and less than twenty washes, tans of the second order and bodies resisting twenty washes, tans of the third order. Of course this is arbitrary and open for convenient modifications. But the expediency of such a classification is obvious. We do not think it is correct to call only bodies of the third order tans, and all bodies of the second order non-tans, as Wilson and Kern do. For if a compound withstands five or ten or fifteen washes under such severe conditions, it certainly must be considered as part of the leather produced. Even if some of these bodies do not precipitate gelatin, they are co-tans of sufficient resistance to washing to be of practical value. The official method on the other hand determines very nearly the sum of all tans proper and co-tans or at least it can be modified so that it will exhaust the solution of all active ingredients. A combination of both methods, with certain amplifications, would probably be a more satisfactory way to measure the valuable constituents of organic tanning materials. As stated at the beginning, however, such a minute analysis of details is only of limited value in the case of the well known types of vegetable extracts. They become of greater value when we deal with less known tanning materials such as syntans. Then such determinations are welcome as a means for comparative

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observations of the tanning properties of vegetable extracts as against the tanning properties of synthetic tans and mixtures of both.

Returning now to our tables we point out first of all the most striking figure, namely that under comparable conditions, hide substance will take up only about 18 per cent of its weight Sorbanol tans of the third order out of same excess of active ingredients as against 53 per cent quebracho tans. This suggests a field for further investigation for the application for light leathers where minimum of weight and complete tannage have to be combined. On the other hand the fact that a certain mixture of Sorbanol and quebracho shows a tannage of 66 per cent against 53 per cent of plain quebracho proves that the vegetable tan and the syntan can be made to work cumulatively. The small percentage of syntan necessary for saturation might be taken as a support of the hypothesis which considers tanning as a chemical combination between the acid group of the tan and the amino group of the collagen, because we have reason to assume that the equivalent weight of the syntan is considerably smaller than the equivalent weight of the vegetable tans. As stated above, however, it would be difficult to explain all observations by any known hypothesis and it is above all a precarious undertaking to apply to colloidal bodies the laws derived from observations on electrolytes. If we change one of more conditions, like the concentration, the proportion between hide substance and tans, the mode of washing, etc., the percentage of tans of the second and third order changes too, in a manner which could hardly be explained conclusively by any hypothesis.

Very instructive are the comparative observations on pure tannic acid. Although consisting of tans proper only the percentage of tans of the second order is relatively higher than under similar conditions on quebracho which consists of a mixture of tans proper and co-tans. This throws some light upon the rôle played by the co-tans as stabilizers and also shows that in the reactions between colloids, the presence or absence of a third body is capable of influencing the reaction taking place between two compounds to a much more decided degree than we are used to observe in reactions between electrolytes.

The Acidity of Synthetic Tans: A great deal has been said against the acidity of syntans. We have dealt with this matter

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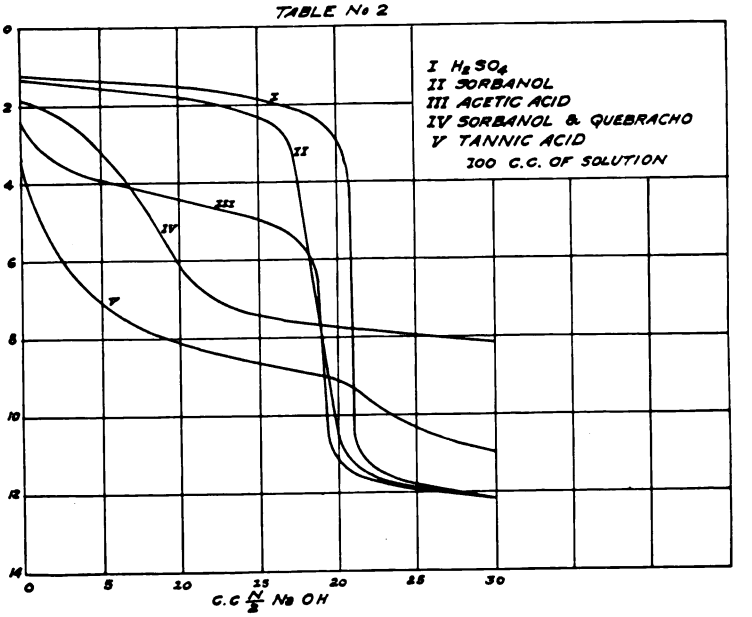
in detail in a previous paper and shall recapitulate here only the main outstanding points. In examining the acidity of syntans it will be of little avail to determine how much of the total acidity is sulphuric acid and how much sulphonic, because there is a greater difference between the various sulphonic acids than between sulphuric acid and some sulphonic acids. Not all sulphonic acids have tanning properties. Furthermore, it is important that we realize that testing a syntan with the hydrogen ion potentiometer or by barium precipitation, or by boiling with hydrochloric acid, etc., can never be as conclusive as testing it on hide substance.

For instance, the point that the active principle of syntans is a sulphonic acid of almost equal strength as sulphuric acid has been over emphasized, but sight was lost of the fact that at least in the case of Sorbanol, the syntan is not used alone but always in conjunction with vegetable extracts. The admixture of the latter



reduces the ionization. This is shown clearly in Table II. While plain Sorbanol has p^H values only slightly higher than sulphuric acid and a very similar neutralization curve, a mixture of quebracho and Sorbanol has a neutralization curve which

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approaches more the general character of a weaker acid as can be seen from the comparison with the neutralization curve of acetic acid and tannic acid.

The view has been expressed that because the active principle of some syntans is a sulphonic acid of about the same p^H value as sulphuric acid, it might, from a practical point of view, just as well be sulphuric acid. This kind of conclusion generalized, would mean that all acids of the same degree of ionizaton behave alike toward hide substance. Although it is rather obvious that such a conclusion is not justified, we suggest a very simple experiment which proves that point conclusively: Take a sample of hide powder, saturate it with vegetable tan (for instance, such as we obtained in our comparative tanning experiments laid down in Table I) and expose it to the action of 50 per cent sulphuric acid. This is about the strength a weak solution of sulphuric acid will dry out to in the open atmosphere. Take a parallel sample of the same hide powder and expose it to the action of Sorbanol of similar concentration. We obtain thus conditions which are similar to those prevailing within finished leather stored away with a content of free acidity, only that we take considerably higher quantities of the acids in order to hasten the effect.

If we remove after a few days, the excess of acid, we find the sulphuric acid has reduced the tanned hide substance to an impalpably fine dust, while a sample treated with Sorbanol retains the structure of the original long fibres.

A similar experiment can be carried out in a few hours, if instead of tanned hide fibres, the less resisting vegetable fibre of cotton fabric, such as cotton gauze, muslin, etc., is taken, and weak solutions of Sorbanol and sulphuric acid are allowed to dry out on the fabric. The sulphuric acid will tender the gauze in a few hours while Sorbanol will leave its tensile strength unchanged even after prolonged exposure.

These two simple experiments prove that the determination of the strength of the acid is not sufficient to predict all functional properties toward other compounds.

Having established this point, the second point is to make sure that the total acidity of the syntan should not be higher than corresponds to its content of the active principle. We have

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shown in our previous paper that the only conclusive way to determine the correct acidity in a syntan is by testing it with hide substance and not with barium, HCl, etc.

After we have made sure of this second point, we yet have to satisfy ourselves that the syntheic tanning acid is not subject to spontaneous conversion into sulphuric acid. Here again we wish to point out a simple and quick test for the stability of the active principle of a syntan: Keep a sample of syntan in a drying oven say at 80° C. until it evaporates to dryness. If the sulphonic acid is of that kind which easily breaks up, the organic base will be set free and the decomposition will betray itself by the appearance of the odor of the base, or by the fact that the residue after evaporation cannot be dissolved again in water. Further if the sample is titrated for total acidity before and after evaporation, the syntan whose sulphonic acid is subject to decomposition will show an increase of acidity because one equivalent of sulphonic acid gives two equivalents of sulphuric acid.

Syntans can be made so stable, that they will stand the evaporation test perfectly, and also will not decompose when heated to boiling with HCl under a reflux condenser. This was noted at the occasion of an attempt to determine the amount of the sulphonic acid of Sorbanol by changing it into sulphuric acid quantitatively. Simultaneously with this observation another very important point was brought out namely, that the quantitative determination of SO_4 ions by barium was impossible in presence of Sorbanol. So great is the dispersion power of this syntan that as insoluble a precipitate as $BaSO_4$ is kept in colloidal solution. This enormous dispersion power is no doubt responsible for its beneficial influence upon the tanning process with vegetable extracts.

Free Acidity in Finished Leather: At present tanners are considerably exercised over the fact that in some cases leather in the tanning of which certain syntans have been used, has deteriorated after prolonged storage. It is probable that this is in part due to the fact that the syntans used, either contained sulphuric acid or were of that variety which spontaneously convert, in time, into sulphuric acid. It is of course preferable to develop and apply methods by which desirable and undesirable syntans can

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be distinguished, rather than test afterwards whether or not the deterioration of the leather is due to sulphuric acid.

The recently proposed provisional method determines all acid radicals capable of forming with soda ash, salts, which will remain neutral upon ignition. It will therefore really determine also hydrochloric acid or phosphoric acid for instance. But since as a rule, sulphuric acid is the only inorganic acid whose presence is likely, the method may prove convenient and accurate for plain vegetable tanned leathers. It is entirely valueless if syntans have been used in connection with vegetable extracts because even the combined sulphonic acids will be partly at least converted into Na_2SO_4 and consequently reported as H_2SO_4.

The ignition method not being available in presence of syntans, we turn to examine the possibilities of leach methods. If leather contains free acids and we leach these acids out with water, the question arises, is the acid contained in the wash water sulphuric acid, sulphonic acid, tannic acid or lactic acid, etc. We are confronted here with a similar problem as in the case of syntan solution and a similar mode of attack will be appropriate. If the hydrogen ion concentration of the wash water is very low, we hardly have to bother with further tests. If the solution shows strong ionization, then it is necessary that we distinguish first, between sulphuric acid and sulphonic acid, and second, (if sulphuric acid be excluded) between sulphonic acids which do and sulphonic acids which do not attack and tender animal or vegetable fibre.

For the distinction between sulphonic acid and sulphuric acid in the wash water, we found Immerheiser's ether method convenient and reliable. For the distinction between harmless and harmful sulphonic acids, our cotton gauze test will prove useful. In a subsequent paper we expect to deal with this phase of the matter in greater detail.

Summary

1. Comparative tanning experiments show that hide substance will take up considerably smaller percentages of syntans than of vegetable tans, out of the same excess of the tanning principle, but if mixed in certain proportions, syntan and vegetable extracts can be made to work cumulatively.

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2. The active principles of syntans are acids of considerable higher ionization than the vegetable tannic acids and very nearly approach the "strength" of sulphuric acid. It is shown, however, that in spite of this fact, syntans have been produced which do not manifest the obnoxious properties of sulphuric acid.

3. Qualitative tests for the distinction between syntans of different properties are suggested.

4. Tests for the identification of the free acidity in finished leather are discussed.

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THE VERSATILITY OF A PLUMPING METHOD *

By H. C. Reed

At the annual meeting of The American Leather Chemists Association, May, 1919, Mr. J. H. Yocum said, "Might I ask Mr. Wilson if he could describe in any quantitative manner the plumping effect of the ions and various acids that exist in tanning liquors, so that one could in a measure be able to estimate the effect of these acids as plumping agents? I mean simply as plumping agents—what their concentrations and efficiencies might be." And later, during the same discussion, "The truth of the matter is that what we want is something that we can use, use in our business, use in every day operations. One of those things is the proper determination and estimation of the plumping action of an acid in the presence of its controllers or electrolytes, or what not, in the tanning liquor. The tanner is quite as anxious as we are to know what the actual plumping value of his acid is, and here we hear 'ionization' and measures of ionization that would require the extremes of laboratory experience by the operators, with a lack of accuracy upon their own parts, and machinery and apparatus that would be wholly impossible."

It appears to me that a plumping method, evolved from the idea originating with Mr. Claflin, may go far in solving the vexed questions presented so forcibly in the remarks of Mr. Yocum just quoted.

* Read at the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Ontario, Canada, June 22, 1922.

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It is the purpose of this paper to show how it may be possible to measure the plumping of an acid liquor, and to at least indicate how extremely versatile a proper method for the purpose can be made to be. It will be my endeavor to present these suggestions from a practical standpoint although it would appear as though ultimately the method may lend itself to the solving of questions of a more highly scientific aspect.

A large amount of research has been done upon the swelling of gelatine in acid solutions, and deductions drawn from the data obtained as to the swelling of hide. It is not my purpose to discuss whether such deductions appear to be justified but it is submitted that conclusions based on results obtained by using a material so closely akin to the basic material of the tanner should have greater weight. Logically it would appear that hide powder should have advantages that gelatine has not. It might be argued that hide should be better for the purpose than hide powder, and in a sense the argument is sound. On the other hand hide is not a material that can be had always ready for use, is not always of a desirable uniformity, is difficult to handle from a laboratory standpoint and can never be a standardized material. Hide powder has none of these objections.

Several methods of measuring the plumping power of acids with hide powder have been suggested. I would refer to the method based on the measurement of the column of hide powder, on the theory that the height of the column directly reflects the measure of the swelling. Such a method may be applicable to a degree in determining the swelling of an acid in water solution, but there are very grave doubts as to its merit in a solution of higher gravity than a water solution of an acid, such as tan liquors. Not only have we in such case to contend with the buoyant properties of the medium in which the hide is suspended but the differences in gravity of the tanned hide powder in comparison with untanned. Recently some considerable work has been done based on the method but with sieved hide powder instead of the hide powder as a whole. I would protest against the use of a sieved hide powder on the ground that sieving, in removing coarser particles of ground hide, may give a product not truly representative of the hide as a whole, for it is con-

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ceivable that certain portions of hide in grinding do not pulverize as readily as others, and the swelling of all portions of hide may not be identical.

A description of the method pursued in making the experiments, the results of which are here given, is in order.

The hide powder used in all tests is the American Standard Hide Powder, 1922, Batch No. 2. For all tests an equivalent of air dry powder representing two (2) grams of absolutely dry powder was used and in all instances 100 cc. of test solution. The theoretical basis of the method depends upon the fact that hide powder in the swollen condition will hold a larger amount of water than when unswollen, and that the amount of water held by the hide powder is a measure of the swelling.

The manipulatory procedure is as follows:— The equivalent of two (2) grams absolutely dry hide powder (hereinafter referred to as two (2) grams powder) is weighed into a six (6) ounce wide-mouthed bottle fitted with rubber stopper. If the solution to be measured for plumping value contains no tannin, 100 cc. of the solution of desired concentration is pipetted into the bottle, stopper inserted, and contents shaken and allowed to stand. The time of contact of hide powder and solution approximated 20 hours in all tests unless otherwise specified. The amount of solution not retained by the hide powder is ascertained by filtration through a cotton plug inserted in the neck of a funnel. The funnel used has a stem not more than from one-half to three-fourth inch long, and the cotton plug is so inserted as to fill the stem. Care must be used not to crowd the cotton, and with water solutions of acids that plump considerably the plug must be very loosely inserted or filtration will be far too slow. A very loose plug can be used if a portion of the plug is allowed to rise within the funnel for on wetting out the cotton will cling to the side of the funnel thus preventing its being forced through the stem. The cotton plug is wet out with water and allowed to drain. The amount of water held by the plug is equal to the amount of acid liquor held, so that the weight of the plug need not be considered. The plug by filling the entire stem of the funnel overcomes the objection of unequal retention of liquor

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in the stem, and the short stem permits drainage without suction, which is necessary since suction would mechanically remove a greater proportion of the menstruum than simple drainage.

The funnel is inserted into a 100 cc. measuring cylinder, the hide powder with test solution poured upon the funnel and allowed to drain until dripping ceases, when the measurement of the amount of solution filtered off is taken.

In all the tests the plumping of the material tested was expressed in ratio to the plumping of distilled water as unity. This was ascertained by swelling two (2) grams hide powder with 100 cc. of distilled water and following the method as described. It was found that maximum swelling of hide powder was reached in three (3) hours and that in twenty (20) hours the swelling was identical and that on filtering 85 cc. of water was drained off, leaving 15 cc. of water retained by two (2) grams absolutely dry hide powder. The standardization of the hide powder with water was the result of a number of determinations agreeing very closely. The method of calculating may best be shown by a typical example. An acid solution returning 75 cc. of solution by filtration would give 25 cc. solution held by the hide powder, and the ratio of plumping would be as 25 to 15 or 1.67. In other words the plumping of the acid liquor is 1.67 times that of water.

Now in the case of measuring the plumping ratio of tannery liquors one has to consider that an element is introduced that is not present in water solutions of an acid, and this is the presence of tannin. For this reason with tannery liquors the procedure must be varied slightly. No tanner would think of introducing a dry hide into a tan liquor and expect to plump it. The case-hardening effect from tanning will prevent swelling. So in testing tannery liquors the hide powder must first be swollen with water. The two (2) grams hide powder are wet out and soaked with the 15 cc. of distilled water which it will retain, the 15 cc. of water being measured into the bottle containing the hide powder. Do not shake the bottle but give it a swirling motion. When the powder is well soaked revolve the wet mass now and then around the sides of the bottle and slap the bottom of the bottle smartly with the palm of the hand to bring the contents well to the bottom. It is well not to allow the

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wet mass to come in contact with the rubber stopper. At the expiration of three (3) hours add 85 cc. of the tan liquor, insert stopper and shake at intervals, allowing to stand over night. Filter in the morning as described.

I have gone into considerable detail as to the manipulative procedure, but in a method of this character necessity demands

TABLE I.—Showing Plumping Ratios of Various Acids.

Normality	Sulfuric	Hydrochloric	Acetic	Butyric	Formic	Lactic	Gallic
0.0005	1.03						1.10
0.00075	1.03						
0.001	1.03				1.27	1.10	1.17
0.002	1.10				1.40	1.20	
0.003	1.10					1.43	
0.004	1.20				1.73	1.60	1.20
0.005	1.33	1.37				1.77	1.20
0.006	1.50				1.93		
0.007	1.63						1.20
0.008	1.73				2.13		
0.009	1.80						1.27
0.01	1.87	2.47	1.47	1.53	2,23	2.20	1.27
0.0125	1.93						
0.015	2.03						1.33
0.0175	2.07						1.33
0.02	2.07		1.77	1.70	2.60	2.57	1.30
0.0225	2.07						1.40
0.025	2.07						1.40
0.0275	2.00						
0.03	1.97				2.80	2.73	
0.04	1.93		2.03	2.00	2.90	2.90	
0.05	1.90	3.07			2.90+	2.93	
0.06			2.17	2.27	2.93	3.00	
0.07					3.03	3.00	
0.08			2.30	2.40	3.03	3.00	
0.09					3.07	3.00	
0.10	1.77	2.53	2.50	2.47	3.07	3.00	
0.15					3.07		
0.2	1.70		2.60	2.73	3.00	3.00	
0.25					2.97		
0.3	1.60		2.67	2.87	2.97	3.00	
0.35					2.93		
0.4	1.47		2.87	2.97	2.93	3.00	
0.5	1.40	1.40	2.87	2.97	2.93	2.97	
0.6			2.87	2.97	2.93	2.97	
0.7			2.87	2.93		2.93	
0.8			2.87	2.93	2.87	2.93	
0.9				2.93		2.93	
1.0			3.00	2.93	2.73	2.87	
1.5			3.00—				
2.0		0.80	2.93	2.60		2.60	
2.5			2.87				
3.0		0.33	2.87				
5.0	Dissolved						

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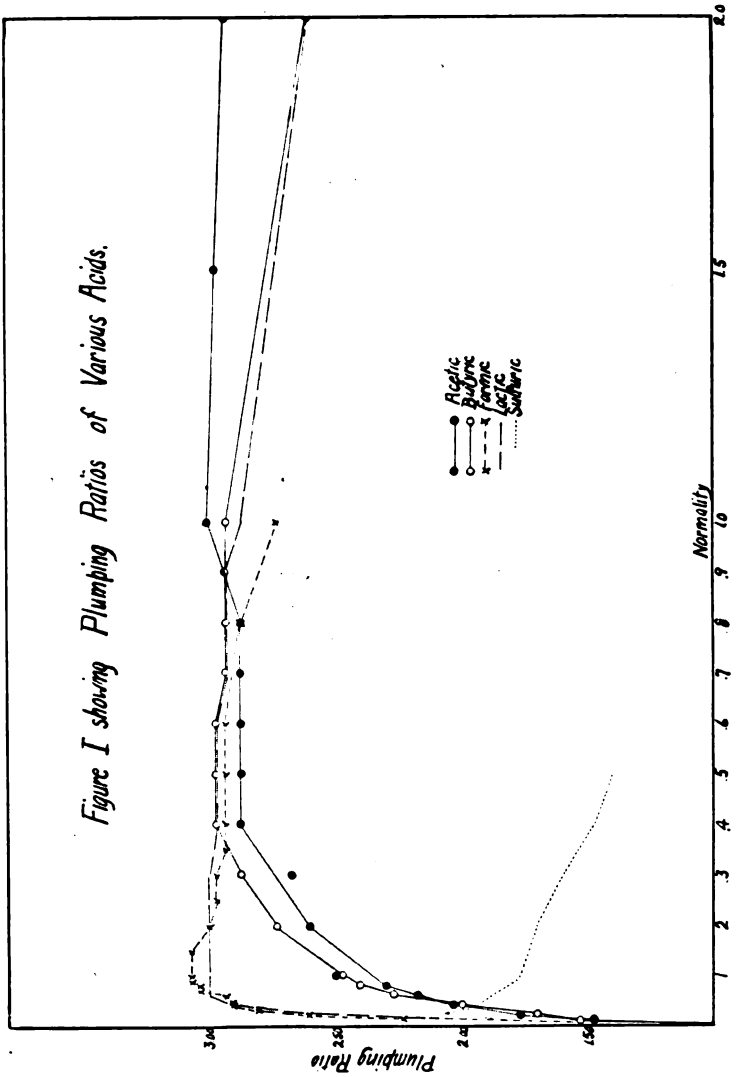

it. A little practice will enable the operator to follow the method with success and I believe he will be more than pleased with the results.

Following the details of the method as given I submit in Table I figures showing the plumping ratio of various acids in water solution, and in Figure 1 the curves plotted from these ratios.

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Reference to the table and curves discloses some very interesting points. The strong mineral di-basic sulphuric acid is quite unlike the weak organic mono-basic acids in plumping value. Sulphuric acid shows a maximum plumping ratio of 2.07 at normalities ranging from 0.0175 to 0.0250 whereas lactic acid has a maximum plumping ratio of 3.00 with normalities from 0.06 to 0.40. Sulphuric acid therefore never will give the swelling that it is possible to get from lactic, and even in very weak concentrations lactic gives a plumping ratio exceeding that of sulphuric. Formic acid is quite similar to lactic in its power of swelling hide powder. The curves as shown in Figure 1 being almost identical, the maximum plumping from formic being a trifle higher than from lactic. On the other hand the two organic acids, acetic and butyric show great similarity in their plumping ratio curves but are quite unlike lactic and formic. While the two latter acids reach maximum plumping ratios of 3.00 and 3.07 respectively at normalities 0.06 to 0.09, butyric and acetic reach their maximums of 2.97 and 2.87 respectively at a normality of 0.40 Also it is to be noted that at 0.01 normality acetic and butyric are distinctly inferior to formic and lactic in plumping value. It is interesting to observe that the mono-basic hydrochloric acid shows plumping far in excess of the di-basic sulphuric, and although sufficient data is not yet at hand to plot the curve for hydrochloric yet from the figures shown it can be predicted that the maximum plump of this acid is at relatively low concentration, probably close to the same normality as sulphuric. Gallic acid has very little plumping value.

There is another very interesting feature of the plumping figures, reflected in the plumping ratio curves, to which I must draw attention. After the several acids arrive at a maximum plumping ratio you will note that the curve becomes practically a straight line and then begins to dip. The dip for sulphuric is much sharper than for the organic acids, and when the curve is plotted for hydrochloric it will prove to have a dip even sharper than sulphuric. In other words, after certain concentrations of acid are exceeded their plumping ratios decrease with the increase in concentration, but the depression in plumping is very gradual with the weak organic acids and particularly sharp in the instance of hydrochloric.

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We note here that sulphuric acid differentiates strongly from the organic acids used as well as from hydrochloric acid in that at all concentrations its plumping power is low. Its maximum plumping ratio is about 2.00 whereas the other acids all show a maximum plumping ratio of about 3.00. This probably is on account of sulphuric acid being a di-basic acid whereas the other acids are all mono-basic. The explanation of this is not clear to-day but it is noteworthy that analogous results have been obtained where mono- and di-valent acids and bases have been compared in their action on gelatine and there is a sharp distinction between the two types.

It is well known that alkalies will plump hide. The measure of the plumping ratio of sodium hydrate is given in Table II and the curve plotted from the Table in Figure 2.

TABLE II.—Showing Plumping Ratios of Caustic Soda.

Caustic Soda		
Normality	Per cent	
.0005	.002	1.07
.001	.004	1.00
.005	.02	1.73
.01	.04	2.00
.02	.08	2.37
.03	.12	2.20
.04	.16	2.13
.05	.20	2.07
.06	.24	2.00
.07	.28	1.93
.08	.32	1.87
.09	.36	1.80
.10	.40	1.63
Saturated lime water		1.20

It would appear as though the maximum swelling with a solution of sodium hydrate was effected with a normality of close to 0.02, the same concentration that produced the maximum swelling in the case of sulphuric acid. The plumping ratio at the maximum is 2.37, greater than shown by sulphuric acid, but less than from the organic acids. With increase in concentration sodium hydrate effects, after maximum swelling is attained, a more rapid depression in swelling than does sulphuric acid. I am convinced that this repression is due to the same cause as the parallel repression in the case of acids in increased concentration, namely hydrolysis of the hide fibre. A somewhat surprising result was gotten with a saturated lime water containing excess

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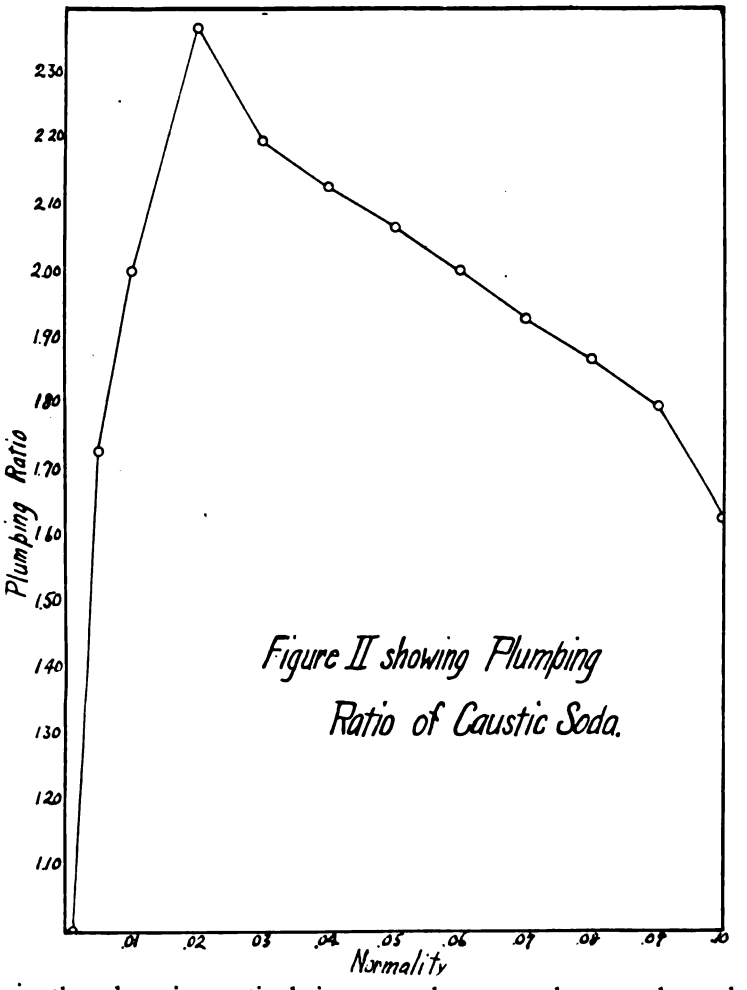

Figure II showing Plumping Ratio of Caustic Soda.

lime, the plumping ratio being very low, 1.20 by actual result. This low swelling value of lime is to be the subject of further investigation. It is possible that under the conditions a repressive action was involved.

A question that is of paramount interest to the tanner and one that has been made the subject of some considerable amount of investigation by chemists, is that of the effect of the presence of salts in tanning. It seemed as though the plumping method might serve to determine and measure the effect of salts upon the

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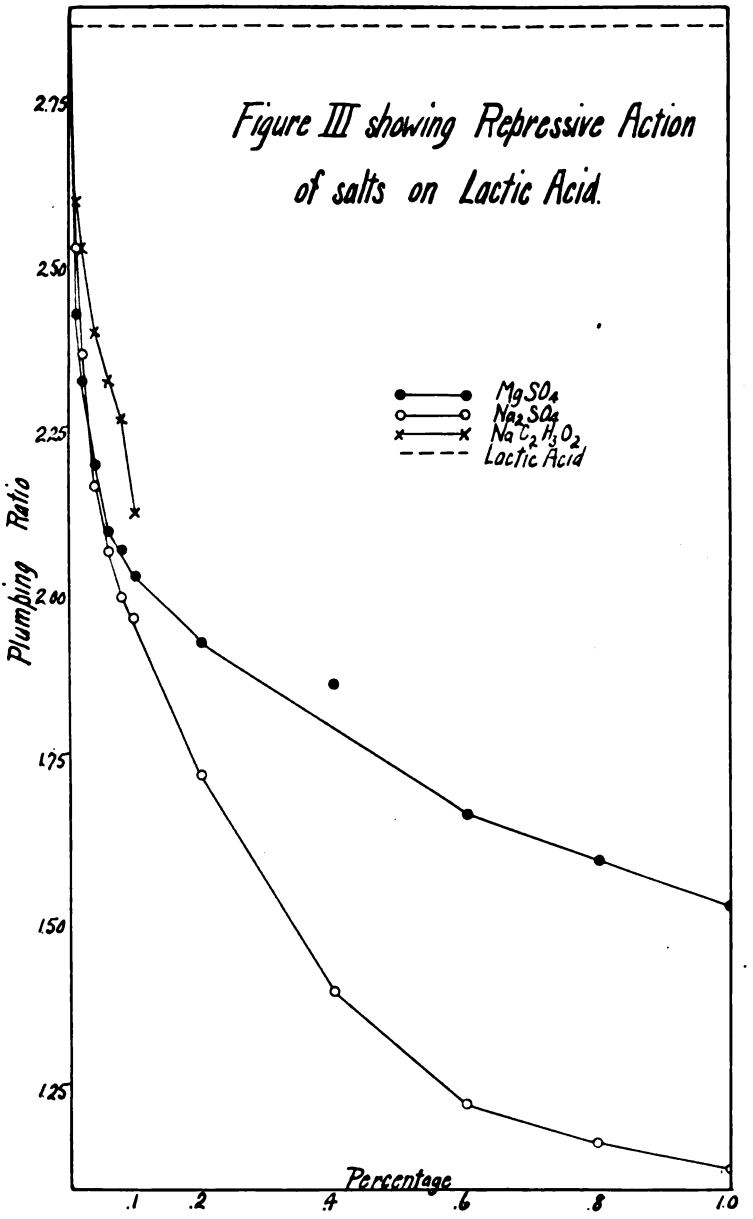

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plumping, so a series of tests were run and the results given herewith. In Table III is shown the repressive action of magnesium sulphate, sodium sulphate and sodium acetate on hide powder swelled to a plumping ratio of 2.87 with lactic acid, and in Figure 3 the curves plotted from the table. Note that the repressive action of sodium sulphate exceeds that of magnesium sulphate in the higher concentrations. Sodium acetate should have been carried to greater concentrations to prove its true repressive effect.

TABLE III.—SHOWING REPRESSIVE ACTION OF SALTS ON LACTIC ACID.

	Lactic Acid		
Per cent	$MgSO_4$	Na_2SO_4	$NaC_2H_3O_2$
.0	2.87	2.87	2.87
.01	2.43	2.53	2.60
.02	2.33	2.37	2.53
.04	2.20	2.17	2.40
.06	2.10	2.07	2.33
.08	2.07	2.00	2.27
.1	2.03	1.97	2.13
.2	1.93	1.73	
.4	1.87	1.40	
.6	1.67	1.23	
.8	1.60	1.17	
1.0	1.53	1.13	

In Table IV is shown the repressive action of salts and of quebracho extract on sulphuric acid. Only a few tests were made but these seem sufficient to prove that the method clearly demonstrates the repressive action of salts on sulphuric acid and that quebracho extract will not repress the swelling of the acid.

TABLE IV.—SHOWING REPRESSIVE ACTION OF SALTS AND EFFECT OF TANNIN ON SULFURIC ACID.

		Sulfuric Acid			
Normality	Per cent	Acid	1 Per cent $MgSO_4$	1 Per cent NaCl	4x quebracho
.01	.049	1.87	1.00	1.00	1.87
.02	.098	2.07	1.33	1.43	2.07
.10	.49	1.77	1.50	1.27	1.77

The solution of quebracho used was four times official strength, or 1.6 grams tannin per 100 cc. approximately 1.4 grams tannin to two (2) grams dry hide powder. The question of the effect of tannin upon swelling will be discussed later.

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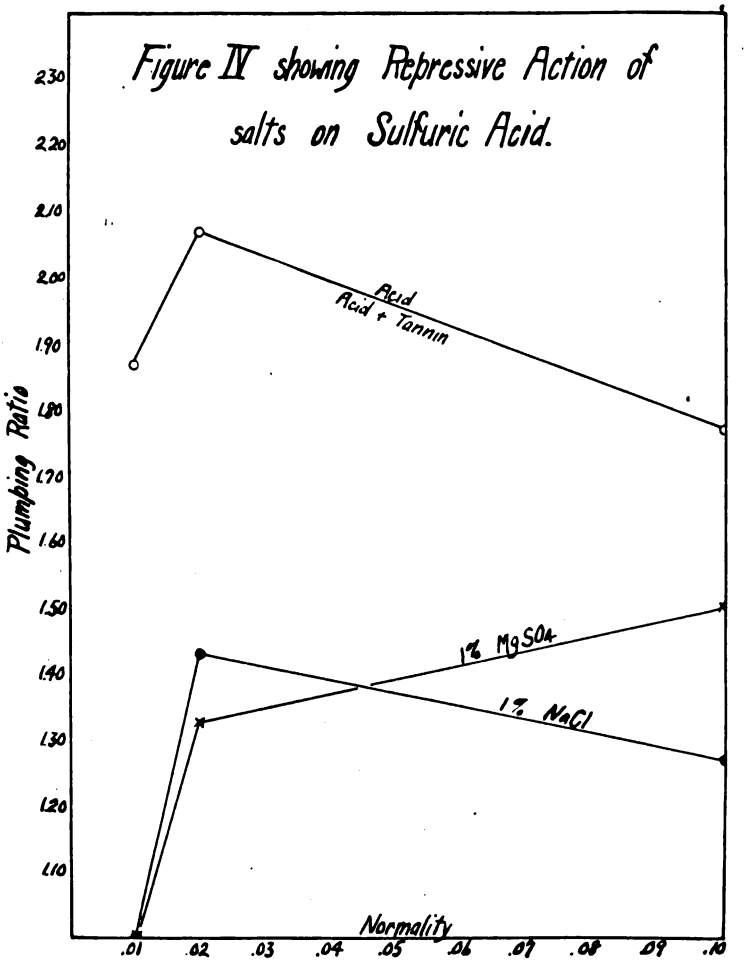

TABLE V.—SHOWING REPRESSIVE ACTION OF SALT ON HYDROCHLORIC ACID.

	Hydrochloric Acid		
Normality	Per cent	Acid	1 Per cent NaCl
.005	0.018	1.37	0.867
.01	0.036	2.47	0.867
.05	0.183	3.07	1.53
.10	0.365	2.53	1.53
.50	1.82	1.40	1.07

In Table V is shown the repressive action of sodium chloride, common salt, upon the swelling of hide with hydrochloric acid.

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There can be no doubt that salt represses the swelling of hydrochloric even though it is claimed that the addition of salt to hydrochloric or sulphuric acid increases the hydrogen ion concentration.

The question of the repressive action of salts on the swelling of hide with acids is a fruitful field for investigation despite the considerable amount of research that has already been done. I feel that at the present time it would be profitless for me to impose any theories that I may hold on the mechanism of the reaction that effects the repression as the investigation has not proceeded sufficiently to warrant conclusions. I would say, however, that indications point to the exceeding value of the plumping method as an aid in solving the problem, that the repressive action of salts on swelling is not hydrolytic as appears to be the case with strong solutions of acids, that on the contrary salts appear to check rather than augment hydrolysis.

It would appear as though sodium chloride differed from magnesium sulphate, sodium sulphate and sodium acetate in its depleting effect on hide swollen in water, as shown in the following Table.

TABLE VI.—Showing Effect of Aqueous Solutions of Salts on Water Swollen Hide Powder.

Per cent	$MgSO_4$	$NaC_2H_3O_2$	NaCl
0.0	1.00	1.00	1.00
0.1	1.00	1.00	
0.2	1.00	1.00	
0.4	1.00	1.00	
0.6	1.00	1.00	
0.8	1.00	1.00	
1.0	1.00	1.00	0.67

You will observe that sodium chloride represses the swelling to a minus plumping ratio of 0.67, while the other salts tested have neither plumping or repressive effect upon the swelling. In other words sodium chloride appears to have a repressive action of its own, foreign to the other salts, quite possibly a function of the chlorine ion as the other salts are sulphates.

The repressive action of salts on the swelling is very prettily shown by the following: Hide powder in 0.06 normal lactic acid gave a plumping ratio of 3.00. An 0.03 normal lactic gives a plumping ratio of 2.73. Now if we reduce the normality of 0.06 normal lactic to 0.03 with a solution of sodium hydrate we

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get a plumping ratio of 1.73 by actual test instead of 2.73. The salt, in this instance, sodium lactate, has repressed the swelling ratio from 2.73 to 1.73. A titration measure of the acid present, such as has been the custom in the case of tannery liquors, would show an acid content corresponding to a plumping ratio of 2.73 whereas the actual plumping ratio was only 1.73.

We know that salts have a repressive action on the swelling of hide with acids. What effect have they upon the swelling of hide with alkalies? This is shown in Table VII.

TABLE VII.—SHOWING REPRESSIVE ACTION OF SALT ON CAUSTIC SODA.

Normality	Per cent	Alkali	1 Per cent NaCl
.001	.004	1.00	1.00
.005	.02	1.73	1.20
.01	.04	2.00	1.50
.05	.20	2.07	1.60

Observe that salts repress the swelling of hide powder with alkalies as well as they do with acids. It can hardly be doubted that salts have a dehyrating effect upon hide whether it be swollen with acids or alkalies. We are aware that sodium chloride has a coagulating effect upon albumens and proteins. Filtrates from hydrochloric acid swelled hide powder gave distinct flocculent precipitates upon addition of salt solution, while corresponding filtrates from hydrochloric acid swollen hide powder repressed with sodium chloride gave little if any precipitate upon addition of salt solution. Flocculation and coagulation indicate expulsion of included water, dehydration. To my mind this is brought about by surface reaction, traceable to the enormous specific surface presented by the colloidal swollen hide. However this is purely speculative and is presented merely as a theory for a working basis.

What is the swelling effect upon hide of acids in admixture? Some idea of this is presented in Tables VIII and IX.

In Table VIII you will note that a 0.50 normal acetic acid solution in admixture with increasing concentrations of sulphuric gave a plumping ratio to all intents identical with sulphuric alone. In other words the stronger sulphuric acid apparently imposes its plumping power to the exclusion of the weaker acetic. In Table IX, admixtures of 0.05 normal lactic and acetic acids, the

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TABLE VIII.—SHOWING EFFECT OF MIXTURES OF ACETIC AND SULFURIC ACIDS.

Sulfuric		Acetic
Normality	Per cent	
	.0	2.87
0.05	0.245	1.93
0.1	0.49	1.83
0.25	1.23	1.67
0.5	2.45	1.50
1.0	4.9	1.27
5.0	24.5	Dissolved

swelling is apparently due to the lactic acid, so long as the lactic is present in large amounts and when the lactic is present in

TABLE IX.—SHOWING PLUMPING RATIOS OF MIXTURES OF ACETIC AND LACTIC ACIDS.

Acids.	Per cent	Actual	Theoretical
100	Lactic	2.93	
75	Lactic	2.83	2.75
25	Acetic		
50	Lactic	2.70	2.57
50	Acetic		
25	Lactic	2.53	2.38
75	Acetic		
100	Acetic	2.20	

Both acetic and lactic acids were 0.05 N.

smaller amounts the acetic assists in the swelling. These results both in the case of the sulphuric plus acetic acids and lactic plus acetic acids are in accordance with the hydrogen ion concentrations we would expect to develop in mixtures of these acids.

A series of tests were run which proved that gallic acid in admixture with lactic acid and in admixture with acetic acid gave the plumping values of lactic and acetic respectively. Gallic acid

TABLE X.—SHOWING PLUMPING RATIOS OF TANNING MATERIALS.

Official strength	Ordinary quebracho	High sulfited quebracho	Closed system chestnut	Open system chestnut	Oak bark	Hemlock bark
½		1.27	1.20	1.23	1.27	1.40
1	1.43	1.40	1.40	1.40	1.33	1.50
2	1.63	1.63	1.60	1.60	1.47	1.73
3	1.80	1.63	1.73	1.77	1.60	1.80
4	1.87		1.83	1.87	1.67	1.87
4½		1.63				
5	1.87	1.67	1.87	1.93	1.67	1.93
5½		1.50				
6	1.87	1.60	1.87	2.00	1.67	1.93
7		1.73				
8		1.80				
9		1.67				
10		1.67				

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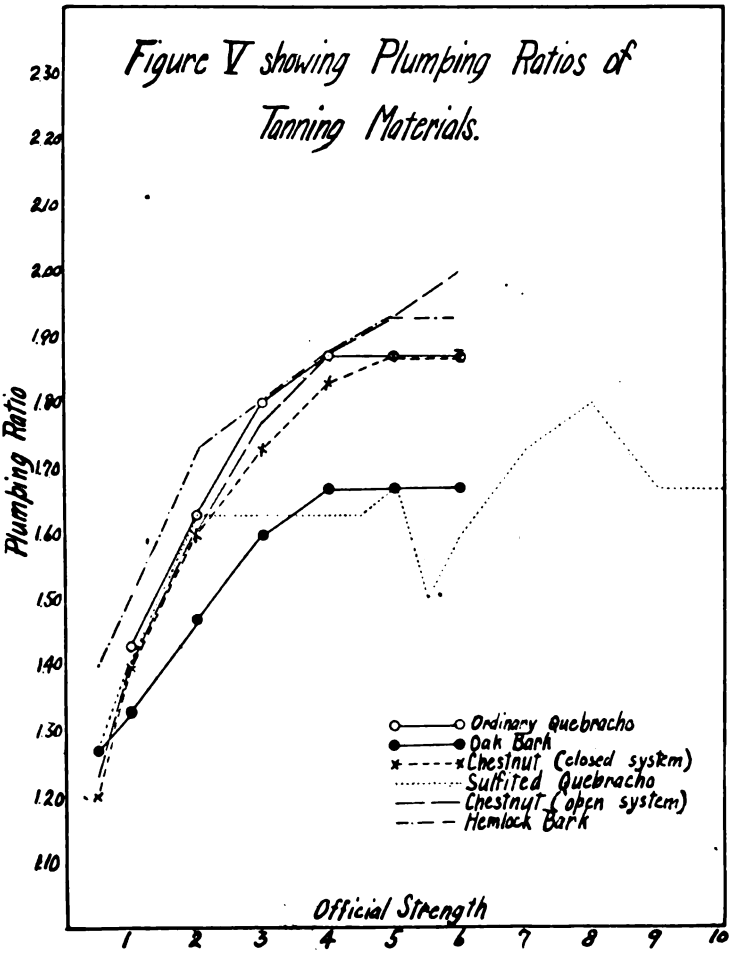
has therefore no influence upon the swelling with lactic and acetic.

Have tannin solutions in themselves any plumping value? I am frank to confess that my conception of a tan solution was that it had a depressing effect upon hide; that the hide contracted. That such is not the case is quite evident from the results shown in Table X with tannin solutions of typical tanning extracts, and the plumping ratio curves plotted from the table shown in Figure 5.



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The results may be criticised on the ground that the extracts themselves contain acids, in the nature of acetic, and that the swelling is due to these acids and not to the tannins themselves. But the argument is without weight in the case of ordinary quebracho extract, which we all recognize as practically free from such acids, and which by actual titration by the gelatine-hematine method, gave negative acid. That tannins have a positive swelling action of their own is confirmed in Table XI, where the results are shown of hide powder first plumped with lactic acid of 0.04 normality and afterwards subjected to progressively increasing concentrations of solutions of ordinary quebracho extract.

TABLE XI.—SHOWING EFFECT OF TANNIN ON ACID PLUMPED HIDE POWDER.

Quebracho Official	Lactic acid 0.36 per cent
—	2.80
¼	2.80
½	2.93
1	3.13
2	3.17
3	3.27
4	3.27

Note that the plumping ratio of 2.80 from 0.04 N lactic acid is increased to 3.27 by an ordinary quebrach extract solution of four times official strength and that the increase in plumping ratio is in direct proportion to the increase in concentration of the quebracho solution. Results are also given when the acid is added to the tannin solution first, shown in Table XII.

TABLE XII.—SHOWING EFFECT OF MIXTURES OF TANNIN AND ACID ON WATER SWOLLEN HIDE POWDER.

Lactic Acid		Ordinary quebracho	
Normality	Per cent	½ official	3 official
—	—	1.47	1.80
.001	.009	1.47	1.87
.0025	.023	1.47	1.87
.003	.027	1.60	1.87
.004	.036	1.67	1.87
.005	.045	1.80	1.87
.0075	.068	2.03	1.97
.01	.09	2.20	2.07
.015	.135	2.43	2.27
.02	.18	2.60	2.33
.03	.27	2.80	2.47
.04	.36	2.90	2.53
.05	.45	3.00	2.60
.06	.54	3.07	2.67

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You will note that when the acid is added to the solution no such plumping effect is attained as when the hide powder is first plumped with acid and the tan added afterwards. In the case of the highly sulphited quebracho extract shown in Table X you will see that the plumping ratio is somewhat irregular, best observed in the curve given in Figure 5 showing the ratio. The results of the first test seemed peculiar but were confirmed by repeat test, and although the complete explanation is not yet available it is suggested that it may be due to depression from the high salt content of the extract. Tests were also run to show the effect in swelling with acid after tanning. The results gave in the case of ordinary quebracho extract identically the same plumping ratio as was obtained with quebracho alone, showing that acid will not plump fully tanned hide powder.

Purely as a matter of interest tests were run by the plumping method as described, using wet hide powder, and by the same procedure but with the use of dry hide powder. The plumping ratio from the wet powder was 1.87 and from the dry powder 1.20. This illustrates well the fallacy of using dry hide powder, and is an instructive commentary on a tannin determination method calling for the use of dry hide powder. The case-hardening effect predominates to the exclusion of swelling.

It would seem, therefore, that we have in the tannins themselves materials that will effect a swelling of hide, and this is amply borne out by results of actual tests with tannery liquors. That the acid determination by titration according to our present official method may but poorly reflect the plumping power of the liquor is evident, but a method of estimating the swelling ability of a liquor gives greater rather than less value to the acid titration method. If for example, a tan liquor shows high acid by titration but low value by the plumping method we feel pretty well assured that it contains substances that are repressive of swelling. If the ash content is high we are quite certain that mineral salts are responsible for the repression. Time did not permit the determination of the effect of organic non-tannin matters on swelling, which would seem of particular importance

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and which should be readily estimated by the plumping method. Should organic non-tans lower the plumping value then, in the absence of salts, depression in swelling could be attributed to low purity.

The effect of salts in repressing swelling in a tan liquor is not a repressive action upon the swelling of the tans, as is evident from the results given in Table XIII.

TABLE XIII.—SHOWING EFFECT OF SALTS ON TANNED HIDE POWDER.

	Ordinary quebracho	
Per cent	$MgSO_4$	$NaC_2H_3O_2$
.0	1.87	1.87
0.1	1.87	1.87
0.2	1.87	1.87
0.4	1.87	1.87
0.6	1.87	1.87
0.8	1.87	1.87
1.0	1.87	1.87

The effect of sodium chloride in the presence of tannin upon the swelling has not been determined, and since it differs from magnesium sulphate, sodium sulphate and sodium acetate in that it represses water swollen hide powder it may have a repressive action when tans are present.

It is perhaps unnecessary to suggest that the plumping method will serve to visualize the repressive influence on the swelling of salts in waters. We have a means at our disposal of valuing waters used for tannery purposes.

There appears from work done with acids to be a very simple explanation of the plumping action, which explanation has been found extremely helpful in co-ordinating the mass of experimental results so far obtained. This explanation is based on the theory of osmotic pressure being the force which causes the swelling, and factors which would increase the osmotic pressure increase the swelling.

Osmotic pressure manifests itself when a sac is suspended in water and a solution of some substance is introduced into the sac, provided the material of the sac has pores large enough to allow water molecules to pass in and out but not large enough to allow the molecules of the dissolved substance to pass.

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In the case of the hide powder the hide powder itself forms the sac and the pores are large enough to allow not only water but dissolved acids to pass in. The acid once it has passed within the sac reacts with the hide substance and brings a portion of it into solution. The molecules of the hide substance are however too large to pass out and hence generate osmotic pressure. The greater the acid concentration the greater will be the amount of hide substance brought into the soluble state and the greater the osmotic pressure developed. This is in keeping with the increased plumping noticed as the acid solution is strengthened. As however the sac is composed of hide substance we must expect that it also is being attacked by the acid and becoming more porous as the action of the acid upon it increases. The result of a more porous sac would of course be the passing out of some of the dissolved hide substance from within and a lessened distension of the sac. It is a question therefore which factor has the greater value, the solubilising of the hide to increase the concentration of the hide substance within the sac, tending to increase the osmotic pressure or the rotting action of the acid on the walls of the sac tending to make it more porous. In the weaker acid solutions we find the first factor the more important and in the stronger acid solutions the latter factor.

In order to check the probability of this explanation determinations of the hide substance in solution at different concentrations were made and the amounts were found to increase as the strength of the acid increased.

Carrying this line of thought still further it would seem that any factor which might be introduced to strengthen our membrane against the attack of the acid would make it more efficient in holding in the dissolved hide substance. This would show in an increased swelling. The figures of Table XI where the powder, fully swelled with acid, was then treated with tannin, illustrate this action and confirm the reasoning. Further it is hard to conceive how the large swelling obtained with tanning materials could arise from their acidity only. It is true that tanning materials contain acids, but in too small amount to account for the swellings shown in Table X. It seems more probable that the membrane is so increased in its efficiency that the smaller amount of dissolved hide within the sac is better retained and exerts its

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pressure to greater purpose than in the cases where acids alone are used to swell.

While the above explanation seems capable of covering the general cases of acids alone or in admixture either with other acids or tanning materials it does not extend to cover the action of salts. Salts repress the swelling but do not, as far as our experience goes, increase the amount of hide substance found in the solution, as found in the case of strong acid solutions. The work is still being carried on to accumulate more data as to the action of salts and it is hoped that a more comprehensive theory will be evolved, which will embrace the action of salts also.

I might say that our present conception of the repressive action of salts is that their dehydrating power is mainly responsible. When the hide powder swells with acid we get a higher degree of dispersion, or a greater number of particles present in the unit volume than originally. Also, since when a particle subdivided into smaller particles occupies more space than the original particle, swelling will prevail. Now these particles are hydrated, that is have water attached and held to them acting as a film separating the particles. When, however, a substance such as a salt is present the hide having a greater affinity for the salt than for the water absorbs salt in preference to water and the hide particles are dehydrated. This causes the particles to come in contact with each other, to coalesce, coadjulate. Thus they will occupy a smaller bulk or the hide swelling will be repressed.

I would like to say a few words on the question of astringency. Just what do we mean by astringency? I think that we all have a sort of general idea but no very concrete definition. If we are to have a method for measuring astringency it would seem plausible to first define what we are going to measure. Again—of what do we desire to measure astringency? The astringency, for example, of a chestnut extract might be one thing and the astringency of the tannin of chestnut quite another. What we really should know, I believe, is the relative astringency of the different tannins in their purified form, since it is probable that what we will call astringency will be subject to modification by relationship with adventitious material such as salts, acids, non-tans, etc. Thus a measure of the astringency of a tan liquor from the yard would be the result of the compensation of the various factors

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that go to increase or decrease astringency. To my mind astringency cannot be divorced from the elements of time; it is a function of time. That is, the astringency of a tanning material is a measure of the degree of tannage produced in a unity of time. There is a possibility that the plumping method may be utilized to show the astringency value and investigation has already been started. I have shown that tanning solutions have a definite swelling value of their own and that this can be measured by the plumping method. The plumping ratios for tan solutions were all determined for a period of time that appeared sufficient for either complete tannage or complete utilization of all tannin present in solution. It seems reasonable to presume that the plumping ratios of a given tanning material in concentration of maximum swelling would vary in ascending ratio with increase in time of contact of hide powder and tan solution. Astringency curves could be plotted. If the theory proves correct the method can be applied to tannery liquors and we shall have another means of ascertaining the condition of yard liquors.

Criticism may be directed against the value of this investigation on the ground that the hide powder is not ash free. This would be a justifiable criticism if the end in view was of a less practical nature. We are attempting to solve some of the many problems that confront the tanner, and in doing so we will hew more closely to the line if we employ the tools that he employs. It is likely that with a small amount of ash in hide powder we are nearer the actual conditions that obtain in practice than if we used ash free hide powder. For more purely scientific investigation there is nothing that mitigates against the use of ash free hide powder, which I have reason to believe can be easily prepared.

In conclusion permit me to say that I recognize how incomplete the investigation is, how meager the subject matter presented when one considers the possibilities. But if I have in small measure succeeded in conveying to you the possible attainments of a plumping method, if I have in any degree inspired you with the desire to investigate and prove to your own satisfaction the versatility of the method,—then I will feel rewarded. At least I think it can be said that the queries propounded by Mr.

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Yocum, quoted at the beginning of this paper, are in a fair way to receive an answer.

I desire to express to Dr. Thomas Blackadder and to Mr. Reeves Hart my appreciation of their assistance in conducting the investigation.

CONTRIBUTION NO. 8 FROM THE REED LABORATORIES.

ABSTRACTS

The Structure of Elastic Gels. By R. H. BOGUE. *J. A. C. S.*, **44**, 1343 (1922). The several theories of gel structure have been reviewed and discussed, and the postulations of the writer that were made in 1920 are repeated and amplified. Many contemporary investigations have been found to support a catenary or fibrillar structure hypothesis, and are set forth.

The premises of this theory are as follows. The sol consists of slightly hydrated or swollen molecules united into short chains. When the temperature falls the threads increase in length and number, and their power of water absorption increases, resulting in an increase in viscosity. A solid jelly results when the relative volume occupied by the swollen molecular threads has become so great that freedom of motion is lost, and the adjacent heavily swollen aggregates cohere. The rigidity is dependent upon the relative amount of free solvent in the interstices of the aggregates, and on the amount of solvent that has been taken up by the gelatin in a hydrated or imbibed condition. The resiliency or elasticity is dependent upon the length and number of the catenary threads, Solution is the reverse of gelation. Swelling is determined by osmotic forces and the Donnan equilibrium.

The influence of electrolytes, of varying hydrogen-ion concentration, and of the valence of the combining ion has been studied upon several of the characteristic properties of gelatin and found to be entirely in agreement and to give additional evidence in support of the theory presented.

Data on the mutarotation of gelatin were found to be in accord with the theory.

The occlusion theory of Loeb is reviewed and found not to be out of harmony with the present theory, but rather to explain the distribution of absorbed water and its variation with hydrogen-ion concentration mathematically in terms of the Donnan equilibrium.

Notes on the Chemistry of Lime Liquors Used in the Tannery. By W. R. ATKIN. *J. Ind. and Eng. Chem.*, **14**, 412 (1922). Lime liquors are "sharpened" by the addition of such substances as sodium sulfide, arsenic sulfide and sodium carbonate in order to hasten unhairing of hides. The addition of sodium salts increases the alkalinity of the lime liquor and also increases the swelling of the hides. No increase in swelling is shown by the use of arsenic sulfide as a sharpening agent as Stiasny has

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shown that the arsenic does not play an important part for it is merely converted in calcium sulfarsenite. It is the formation of calcium sulfhydrate which increases the unhairing action of limes "sharpened" with sulfides.

The increased swelling obtained with the use of sodium salts is explained by the theories of Procter and Wilson and of Loeb by the formation of sodium collagenate which has a greater osmotic pressure than calcium collagenate. It is for the same reason that the addition of common salt to the lime liquors increases the swelling. The author states that a large sole leather yard in England successfully obtain increased swelling and plumping in the limes by using the salt is already in the hides, not washing it out before liming.

The Manufacture of Animal Materials into Gelatin and Glue. By R. KISSLING. *Chem. Ztg.*, **46**, 113 and 151 (1922); *C. A.*, **16**, 2428 (1922). A review, with numerous German patent references, of the manufacture of gelatin and glue from hide and leather scrap, hides, bones, fish scrap, and cadavers of animals.

Studies in Chrome Tanning. Equilibria between Tetrachrome Collagen and Chrome Liquors. The Formation of Octachrome Collagen. By A. W. THOMAS and M. W. KELLY. *J. Ind. Eng. Chem.*, **14**, 621 (1922). Chromed hide powder was prepared which gave results on analysis that were slightly higher than the tetrachrome value. Portions of this dry chromed hide, representing 5 grams of dry hide substance, were covered with 200 cc. portions of freshly prepared chrome liquors of varying strengths (eleven solutions varying from 0.43 to 208 grams of Cr_2O_3 per liter). After contact of eight and one-half months the tanned powders were analyzed. The results show that tetrachrome collagen is hydrolysed slightly in water and in the first dilute chrome solution. The other solutions all give leather containing greater amounts of Cr_2O_3 and SO_4 than the original. From the most dilute solution there is a steady increase in the amounts of Cr_2O_3 and SO_3 adsorbed to a maximum which is obtained in a solution between 7.8 and 15 grams Cr_2O_3 per liter. After this point there is a gradual decline in the amounts absorbed. An identical experiment was run at the same time using dry hide powder. While the curves showing adsorption of Cr_2O_3 and SO_3 for this experiment are somewhat similar to those reported previously for a 48-hour period the amounts adsorbed are somewhat greater. In this experiment an octachrome collagen is obtained in a solution of the same concentration as produces a tetrachrome collagen in 48 hours. The authors claim that these results lend additional support to their belief that the combination of chrome with collagen is strictly a chemical reaction.

A Method for Determining the Surface of Adsorbent Powders. By F. PANETH. *Zeit. f. Elektrochemie*, **28**, 3456 (1922) through *Coll.*, **624**, 124 (1922). In order to determine whether a coating of adsorbed material is one or more molecules thick the surface area of the adsorbent must be known. The author determined this for lead sulfate (or lead chromate) by shaking this salt with a radioactive isotope, Thorium B, and determining

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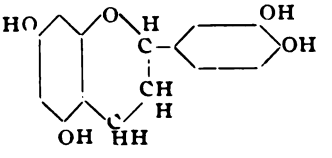
the amount of the latter which was adsorbed. After equilibrium is established between the thorium adsorbed on the surface of the lead and that in solution, this ratio is the same as that of the lead on the surface of the salt to the lead in solution.

$$\frac{\text{Isotope absorbed}}{\text{Isotope in solution}} = \frac{\text{Element on surface}}{\text{Element in solution}}$$

The ratio of isotope adsorbed to isotope in solution was found by determining the radioactivity of the solution before and after the adsorption, while the lead in solution was determined by the usual methods. The lead on the surface could then be calculated. Of one gram of lead sulfate 9.10^{-4} grams of the lead, or about one thousandth of the total, was found to be on the surface. In an adsorption experiment with the dye, Ponceau 2R, and lead sulfate one molecule of the dye was found to lie on about eleven molecules of lead sulfate and considering the densities the surface of the lead was about 31 per cent covered. In case the dye molecules are flat instead of cubical more of the surface would of course be covered. This agrees with the view that a mono-molecular coating is the thickest coating that can form. I. D. C.

Stereoisomeric Catechin. II. By K. FREUDENBERG, O. BÖHME and L. PURRMAN. *Coll.*, **624**, 98-108 (1922). Recent work has shown (*Berichte*, **53**, 1316 (1922); **54**, 1204 (1922)), that catechin is derived from one of the two forms I or II by replacement of one hydrogen by a hydroxyl group.

I



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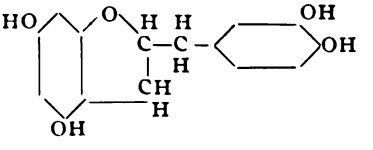

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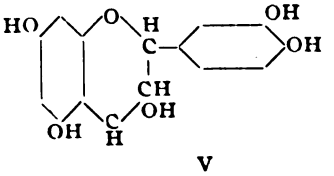

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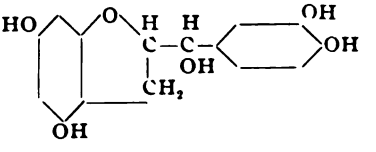

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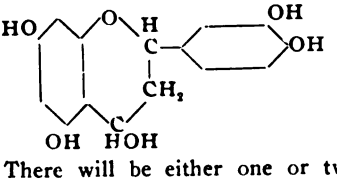

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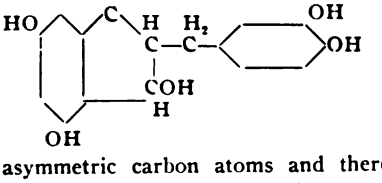

There will be either one or two asymmetric carbon atoms and therefore one or two racemates, depending on whether the hydroxyl group is

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or is not attached to the bridge carbon atom. It has been found that *d*-catechin could easily be rearranged to the *d*, l-catechin and this method of rearrangement was used in the search for the possible new racemate. It was considered impossible to separate four active components from a mixture so the *d*, l-catechin, formed by mixing Uncaria gambier and Acacia catechu (see *Ber.*, **54**, 1204) was used since this could change only to the new racemate. Twenty grams of the *d*, l-catechu was heated in a stream of hydrogen or carbon dioxide with 600 grams of saturated salt solution for 10 hours. It was then extracted with ether and the ether residue taken up in a little water and allowed to crystallize. *d*, l-catechu was separated and identified by its melting point and by forming the penta-acetyl derivative. Another compound also crystallized out and was called *d*, l-epicatechin. Pegu catechin (the crude concentrated sap of the wood of acacia catechu) was extracted with ether and the ether extract dissolved in water and fractionally crystallized. There was obtained first *d*, l-catechin, then some pure l-catechin with a rotation of —17° in aqueous acetone, and also some l-epicatechin having a rotation in aqueous acetone of —38° and in alcohol of —42°. The *d*, l-epicatechin separated out last. The l-epicatechin was slightly more soluble than l-catechin and was also strongly optically active in alcohol while l-catechin was inactive. l-Catechin is probably the principal constituent of catechu, the other isomers being formed during extraction. Catechu is very unstable toward heat, the greater part of it being changed to an amorphous tarry tannin during the heating with the salt solution. That the l-epicatechin was really a component of *d*, l-catechin, while not definitely proven, was very probable since the properties of l-epi- and *d*, l-epi- parallel those of l- and *d*, l-catechin. That *d*, l-epicatechin is a stereoisomer and not a structural isomer is probable since four racemates would be possible if a structural change took place and only two isomers have been found. Stereoisomerism is the simplest and a sufficient explanation for all of the compounds found so far. The possible forms if there is a structural change are shown in Figures 3 to 6. The properties of some of the methyl and acetyl derivatives of the isomers are given. The *d*-catechin gave the following reactions with gelatine; a strong precipitate was formed by mixing equal parts of 1 per cent solutions or by mixing 8 cc. of 5 per cent catechin with 5 cc. of 0.5 per cent gelatine. On mixing 1 part of 1 per cent catechin with 2 parts of 0.5 per cent gelatine a turbid solution resulted which gave a precipitate on cooling below 10°. No precipitate formed when equal parts of 0.5 per cent solutions were mixed. With brucine a compound of one molecule brucine and one molecule of *d*-catechin was formed which was difficultly soluble in cold water and was less soluble in hot water than the catechin.

I. D. C.

Leather Investigations. By L. JABLONSKI. *Coll.*, **623**, 53; **624**, 96 (1922). An address delivered before the German section of the I. A. L. T. C. For the work presented here thirteen bark tanned, unfinished B. A. ox hides were used and determinations were made of moisture, nitrogen,

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and specific gravity. The samples for analysis were taken from around the edges and from two places in the center. The results are given only by means of curves. Variation in specific gravity in all of the hides was very similar and regular except in the shanks. One side of a cow hide was completely worked up and it was found that the specific gravity increased from the belly almost to the backbone and in the other direction towards two lines drawn so as to divide the side from shoulder to tail into three equal sections. In general the percentage of nitrogen increased as the kidney section was approached. The other side of this cow hide was rolled before testing and the specific gravity was therefore higher and less regular. In a loaded cow hide the leather around the edges had the highest specific gravity and water soluble content.

The section of the hide from which a piece of leather had been taken could be determined microscopically even after the leather had been rolled. A series of micro-photographs are given which show the appearance of the fibers. One section for photographing was cut in the head-tail direction and the other in the backbone-belly direction. In the *butt* the fiber bundles are thick and many celled and almost all lie in the head-tail direction. In the *neck* the fiber bundles are smaller and the two sections have about equal numbers of parallel and crossed fibers. In the *tail* bundles are almost as strong as in the butt, but are plainly tangled. In the *belly* the bundles gradually become smaller, changing to single fibers, and fewer are parallel. It is stated that not only could the section of the hide be determined but also the sex and often the breed of the animal. Some portions of hide having a fine fibered structure were found to be gelatinized, although to the naked eye the leather was of good quality. This may explain why belts, etc., occasionly break although they seem to be strong. I. D. C.

Tanning-Chemical Investigation of Proteins. By W. MOELLER. *Zeitschr. für Led. u. Gerb. Chem.*, 1, 188 (1922). Tanning chemistry of the last thirty to forty years has proceded on the assumption that the composition of hide used in tanning consisted either of a single uniform substance or a mixture of closely related constituents, although previous investigators had stressed the heterogeneity of corium and especially refer to an intercellular substance. The attitude of the recent investigators is attributed to a complete neglect of histology of the hide. We need only to turn to text books of histology or biochemistry to be impressed with the difference in the various constituents of corium. Thus in the work of Unna (*Biochemie der Haut*, 1912) there is given about a dozen different constituents of raw hide, which act differently toward the numerous reagents and are different in composition. Besides collagen we know of the existence of elastin and other so-called, true proteins, as hide muscles, nerve and blood vessels, feeding and wandering cells, etc. All of these exert a definite influence and contribute to the properties of various kinds of leather.

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This article is confined to an investigation of the action of certain acids, alkalies and tanning substances on blood fibrin as a representative of the true proteins. *Hydrochloric Acid*: One thousand cc. of N/10, N/2 and N/1 solutions of hydrochloric acid were used for time intervals of 8 days, 14 days, 3 weeks and 4 weeks. It was found that fibrin was decomposed but little in the N/10 acid solution, from 3.5 to 4 per cent being found in solution while the water blank gave about 1.2 per cent. There was practically no increase in hydrolysis for increased time of contact in this strength acid solution but as the concentration of the acid was increased, hydrolysis of the fibrin increased both for increased concentration and increase in time. *Caustic Soda*: Caustic soda has an exceedingly strong hydrolytic influence on fibrin and this protein proves to be much less resistant to caustic soda than the collagen fiber. Even in N/100 solution, much fibrin was hydrolysed. In N/1 solution it was completely dissolved in 8 days. The hydrolysis increased greatly with increase in time of contact and increase in concentration.

Tannin Solutions: Blood fibrin was treated with about a 2 per cent quebracho tannin solution for time periods of 8 days, 14 days and 1 month. It was found that relatively smaller percentages of tannin were adsorbed than was found under the same conditions with hide powder and it is concluded that this is owing to the tannin being adsorbed merely by the surface of the fibrin fibers. The amount of fibrin hydrolysed by the quebracho solution for the 8-day and 14-day periods corresponded with the water value but for the 1 month period there was a considerable increase. Corresponding tests made with a tannic acid solution of about 2 per cent strength gave practically the same results.

Chrome Alum: Corresponding tests were made with solutions of chrome alum containing about 2 per cent Cr_2O_3. One set of experiments was made with a neutralized solution and the other with an acid solution. It was found that both solutions gave an increase in adsorption of Cr_2O_3 with increase in time of contact. With the acid solution there is an apparent stop in the adsorption after 14 days with a decrease in the amount adsorbed for the one month time period. While the neutral solution gives a continual increase with every indication that the maximum adsorption is not reached at the end of 1 month, considerably larger amounts of Cr_2O_3 are adsorbed by fibrin than was found to be the case with collagen fibers and the rapidity of the adsorption by the former is greater. The hydrolysis in both solutions is greater than the water value but is constant for the different time periods. *Formaldehyde*: Owing to the difficulties of accurately determining the formaldehyde adsorbed the author does not consider the figures given as reliable but believes that more formaldehyde is combined with the fibrin than was found with hide powder. *Calcium Hydroxide*: While solutions of calcium hydroxide exhibit the same general tendency to decompose fibrin as shown by caustic soda, its action is not so great. The hydrolytic action of solutions of calcium hydroxide on fibrin is much greater than its action on hide powder under the same conditions.

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The author advocates the belief that these investigations throw some light on the claim that the amount of the so-called true proteins (containing tyrosine and phenylalanine) such as elastin, contained in a hide should determine whether it is to be used for upper or sole leather and also should determine the beam house treatment a hide is to receive. It is believed that a high percentage of elastin is desirable in hides for sole leather to give firmness and the opposite in upper leather. G. W. S.

The Tanning-Chemical Action of the Sulfo-Group Artificial Tannins II. By W. MOELLER. *Zeitschr. für Led. u. Gerb. Chem.*, **1**, 203 (1922). An investigation of the tanning properties of some commercial synthetic tannins using the methods described in the previous articles on the same subject. [*Coll.*, **607**, 560 (1920) *and Zeitschr. für Led. u. Gerb. Chem.*, **1**, 100 (1921). See Abstracts, This JOUR., **16**, 167 (1921) and **17**, 251 (1922)].

The materials investigated were those appearing under the names of Carbatan, Esco, Korinal, Wormatol and a sulfite cellulose extract. These materials in contrast with those previously reported on showed little or no hydrolytic action on hide powder. When leather, which was tanned with these materials, was subjected to Fahrions boiling test results were obtained that were somewhat analogous to those obtained with other synthetic materials with several exceptions. These results were as follows:

BOILING TEST OF LEATHER TANNED WITH ARTIFICIAL TANNING MATERIALS

Kind of syntan	Hide substance in dry leather	Total soluble in in test as per cent of dry leather	Hide substance in solution as per cent of dry leather
Carbatan A	48.38	25.00	7.06
Korinal	60.18	28.53	16.90
Wormatol	56.09	35.52	20.53
Esco-extract	68.95	12.08	3.30
Sulfite cellulose extract	71.15	93.54	62.02

The leathers made with Esco-extract and Carbatan A when subjected to this test give results which compare favorably with those obtained on vegetable tanned leather. Korinal and Wormatol give results which approach those previously reported for Neradol and Ordoval while the sulfite cellulose extract cannot hold any claim to a tanning material since the leather formed by it is completely decomposed when subjected to this test. The author claims that the sulfite cellulose extract used is a commercial product which is purified and prepared especially for tanning purposes. G. W. S.

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ASSISTANT CHEMIST—Experience in the making of analysis and color tests and in experimental tanning and leather work. For information communicate with Secretary.

MEETING OF THE LEATHER DIVISION OF THE AMERICAN CHEMICAL SOCIETY

The Leather Division of the American Chemical Society held its meeting September 6th and 7th at the Convention of the Society in Pittsburgh when the following papers were presented:

JOHN ARTHUR WILSON and GUIDO DAUB: The Mechanism of Unhairing.

JOHN ARTHUR WILSON and ALBERT F. GALLUN, JR.: Pancreatin as an Unhairing Agent.

CHARLES S. HOLLANDER: A Study of the Strength of Proteolytic Enzymes in the Process of Bating.

ARTHUR W. THOMAS and FRANK L. SEYMOUR-JONES: The Hydrolysis of Collagen by Trypsin.

JOHN ARTHUR WILSON and ALBERT F. GALLUN, JR.: The Points of Minimum Plumping of Calf Skin.

JOHN ARTHUR WILSON and ALBERT F. GALLUN, JR.: Direct Determination of Plumping Power of Tan Liquors.

JOHN ARTHUR WILSON and ERWIN J. KERN: Effect of Hydrogen Ion Concentration upon the Analysis of Vegetable Tanning Materials.

JOHN ARTHUR WILSON and ERWIN J. KERN: Stability of the Hide-Tannin Compound at Different P_H Values.

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MARGARET W. KELLY: The Concentration Factor in the Fixation of Tannins by Hide Substance.

MARGARET W. KELLY: The Hydrogen Ion and Time Factors in the Fixation of Tannins by Hide Substance.

ARTHUR W. THOMAS and MARGARET W. KELLY: The Influence of Neutral Salts upon the Fixation of Tannins by Hide Substance.

ARTHUR W. THOMAS and MARGARET W. KELLY: The Difference in Kind or Degree of Tannin Fixation as a Function of Hydrogen Ion Concentration.

ARTHUR W. THOMAS and ALEXANDER FRIEDEN: The Tannin-Gelatin Reaction.

ARTHUR W. THOMAS and STUART B. FOSTER: Are Vegetable Tannins Amphoteric?

R. O. PHILLIPS and L. R. BROWN: The Practical Color Measurement of Vegetable Tan Liquors.

S. KOHN, J. BREEDIS and E. CREDE: The Acidity of Synthetic Tans.

FRANK L. SEYMOUR-JONES: The Colloid Chemistry of Basic Chromic Solutions.

FRANK L. SEYMOUR-JONES: The Electrophoresis of Chromic Solutions.

EDMUND STIASNY: Some Modern Problems in Leather Chemistry.

JACQUES LOEB: The Interpretation of the Influence of Acid on the Osmotic Pressure of Protein Solutions.

S. E. SHEPPARD and S. S. SWEET: A Preliminary Study of a Plunger Type of Jelly Strength Tester. (Lantern).

S. E. SHEPPARD and S. S. SWEET: The Anisotropic Swelling of Thin Sheets of Gelatin. (Lantern).

S. E. SHEPPARD, F. A. ELLIOTT and MISS A. BENEDICT: The Preparation of Gelatin Free from Ash and Hydrolytic Decomposition Products.

E. BATEMAN and G. G. TOWN: The Hygroscopicity of Hide Glues and the Relation of Tensile Strength of Glue to its Moisture Content.

JOHN ARTHUR WILSON and ERWIN J. KERN: The Two Forms of Gelatin and Their Isoelectric Points.

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The next meeting of the Leather Division will be held in Milwaukee in September, 1923. The following were elected to serve as officers of the Leather Division for the next year—Chairman, John Arthur Wilson; Vice-Chairman, Charles S. Hollander; Secretary-Treasurer, Arthur W. Thomas; Members of the Executive Committee, C. R. McKee and F. P. Veitch.

THE INFLUENCE OF ATMOSPHERIC HUMIDITY ON THE STRENGTH AND STRETCH OF LEATHER *

By F. P. Veitch, R. W. Frey and L. R. Leinbach

Introduction

It has been clearly shown by a number of investigations that the relative humidity of the air materially affects the physical properties of many materials, especially those of a fibrous nature. Most textbooks dealing with the physical properties and with the testing of materials, however, either ignore this important fact or treat it incidentally.

Few accurate and extensive data showing the effect of atmospheric humidity and the moisture content of leather upon its strength and stretch have been found. Rudeloff[1] in anticipation of the importance of the subject made some experiments at various relative humidities, using two strips of chrome leather, two strips of oiled leather, three pieces of belting leather and two pieces of vat-tanned leather. In all only fifty-six test pieces were used, so that in distributing these over the numerous humidity ranges mentioned extensive data for any one condition could not be obtained. The tests also were not strictly comparable with respect to position in the hide, although an effort was made to eliminate this variation as much as possible. For studying the absorption of moisture, Rudeloff worked at the following humidity changes: 52.5 per cent to 87 per cent; 46 per cent to 65 per cent; 60 per cent to 81 per cent; and 52.5 per cent to 95 per cent. For adjustment from a higher to a lower humidity he tested at the following conditions: 82 per cent to 60 per cent; 82 per cent to 65 per cent; 65 per cent to 50 per cent; and 56 per cent to 23 per cent. No mention is made of temperature control, and it is

* Read at the Nineteenth Annual Meeting of the A. L. C. A., at Bigwin Inn, Ontario, Canada, June 21, 1922. Published by permission of the Secretary of Agriculture.

[1] *Mitteilungen K'gl., Materialprüfungsamt Gross-Lichterfelde*, 1904, *Hft.* 1-2.

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evident from the text that the humidity control at the high conditions was not very rigid. A cellar was used for exposure at 87 per cent relative humidity, and at 65 per cent and 95 per cent closed vessels of moist air were employed for conditioning, the humidity in the vessels being determined by hair hygrometers. Only the samples which were conditioned at 65 per cent and 57 per cent relative humidity were tested in the same room where they were kept, the others consequently undergoing a change while being tested.

Rudeloff concludes from his work:

"(1) That the absorption and liberation of moisture takes place very rapidly with changes in relative humidity, but several days (as many as eight for some leathers) are necessary for complete adjustment;

"(2) That complete adjustment occurs more rapidly upon giving up of moisture than upon absorption from the air;

"(3) That thick leather requires a longer time than thin leather for equalization of moisture;

"(4) That with the same relative humidity chrome leather has a higher moisture content than does ordinary belting leather;

"(5) That leather exposed to the air until equilibrium is reached has with lower relative humidities a proportionally lower moisture content but with higher relative humidities the tendency to take up moisture from the air increases, especially with chrome leather;

"(6) That with increasing moisture content leather expands, and even noticeably so with a low moisture content;

"(7) That under the same load dry leather shows a greater per cent stretch than does moist leather;

"(8) That the tensile strength of chrome leather steadily increases with increasing moisture content up to about 50 per cent; with a higher moisture content the strength apparently decreases.

"The tearing length with respect to the moisture content apparently reaches its highest value at 30 per cent. With belt leather the proportion appears to be about the same but the influence of the moisture is less apparent on account of the lower moisture content of such leather."

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Among other things Rudeloff points out that "since the moisture content and the tensile strength of leather rapidly change with changes in relative humidity, strength tests should be made when the leathers have as near as possible the same moisture content. It is shown, however, that different leathers exposed under the same relative humidity absorb different amounts of moisture, and it is therefore impracticable to bring all the samples to the same moisture content before testing. Under such circumstances the only procedure is to expose the samples before testing to a definite humidity condition until they have come to equilibrium and then after testing to determine the actual moisture content of the leather and record it along with the strength test results. The normal relative humidity for testing conditions should be fixed at 65 per cent to 70 per cent and to insure equilibrium without repeated weighings the samples should be exposed to these conditions for eight days before testing."

Paessler,[2] in extended experiments on the strength of belting leather, attempted to avoid complications due to humidity by conducting all physical tests after conditioning the leather in a humidity room.

Roys[3] has recently shown the commercial importance of the effect of relative humidity on the stretch of leather belting. He concludes that the modulus of elasticity of the belt is different for different relative humidities; that for a given change in tension the stretch is greater at a high than at a low humidity; and that for a given change in humidity the stretch increases with the tension.

Plan of Experiments

Because of the time required for leather to reach practically complete conditioning and because of its tendency to rather quickly undergo some change immediately upon exposure to different conditions, experiments on the effect of humidity must be made entirely within a room in which the relative humidity is rigidly controlled and maintained continuously. Any intermittent conditioning or conditioning in one room and removing to another for testing is open to grave question. In order to supplement and extend the meager and possibly questionable data, ad-

[2] *Collegium*, Nos. 345, 346, 347, 348, 349, 350 (1909).
[3] *Hide and Leather*, Jan., 1, 1921, p. 21.

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vantage was taken of the exceptionally favorable facilities for such work and the effect of different percentages of humidity on the tensile strength and stretch of leather was determined with the utmost care. The results of the first of these studies which cover the effects of three rather widely different but not extreme relative humidity conditions, on vegetable tanned calfskin, are embodied in this paper.

Testing Room: The special constant temperature—constant humidity room of the Bureau[4] which is controlled and maintained day and night was used. The condition of the room is automatically charted by a hygrothermograph and during the experiments it was frequently checked by a sling psychrometer. This room will be referred to hereafter as the humidity room, to distinguish it from the laboratory.

Machine Used: The tensile strength machine used for this work was a 200 kg. capacity Scott tester of vertical type. It was therefore necessary to select rather light leather for the experiments. It was also necessary to use small test pieces. This, however, was an advantage, since a large number of test pieces could be obtained and each pair for comparison was less subject to the effect of position in the skin, because of their small size. The Scott tester was equipped with an attachment to align the jaws and with guides, devised in the laboratory, to insure the insertion of the test piece in a vertical position. All pieces were broken on the same machine by the same operaters.

Leather Used: Three sides of vegetable-tanned kip leather, free from imperfections and as uniform in thickness as possible were selected. These sides were from the same lot of skins and went through the tannery at the same time. They were taken from the tan liquor, scoured and finished by setting out well, but not rolled or jacked. No oils, greases, finishes, or sizes were used. In other words, the sides were finished in the "crust." Analyses of representative samples of the sections used for the strength test are given in Table I. It will be noted that the sides are unloaded and but lightly tanned. From an experimental viewpoint they might be considered "pure" leather.

[4] *J. Ind. Eng. Chem.*, 10, 38, 1917.

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TABLE I.—CHEMICAL ANALYSIS OF SECTIONS USED FOR STRENGTH TESTS.
(All results on moisture-free basis)

L. and P. No.	38,893	38,894	38,895
Side No.	3	4	5
Insoluble ash (assumed)	0.30	0.30	0.30
Petroleum ether extract	0.16	0.14	0.32
Soluble solids	5.31	6.05	6.89
Hide substance	60.98	60.26	55.01
Combined tannin	33.25	33.25	37.48
Degree of tannage	54.53	55.18	68.13
Total ash	0.63	0.61	0.70
Epsom salts	—	—	—
Glucose	0.19	0.19	0.14
Soluble tannins	2.50	3.03	3.63
Soluble non-tannins	2.81	3.02	3.26
Acidity, P and S	0.97	0.81	0.77

Plan of Testing: From each side a section about 66 cm. by 45 cm. was cut from what is considered the prime portion. Each section was laid off into six strips, 11 cm. wide, at right angles to the backbone line. Each strip was marked off into thirty *blocks*, 1.5 cm. wide, the blocks running parallel to the backbone line. The layout is illustrated in Figure 1.

A *test piece*, exactly 10 cm. by 1 cm., was cut from each 11 cm. by 1.5 cm. block by means of a die. Before dieing out, the test pieces were numbered, the number being always placed toward the head end of the side. Thus one hundred and eighty test pieces were obtained from each section of each hide. The thickness of each test piece was measured in thousandths of an inch at three points equally spaced between the breaking length of the test piece. The thickness measurement nearest the point of rupture was then taken in calculating results. Thickness measurements on all test pieces were made in the laboratory and then, as a check upon any ordinarily measurable changes in thickness while conditioning in the humidity room, every tenth piece was again measured at the conditions tested. It was found that there was no appreciable change, as shown by the following figures, which differences are well within the limits of error for the usual measurement of thickness.

				Per cent of value found in laboratory
Thickness at	35%	relative humidity for	Side 4	99.7
Thickness at	35	relative humidity for	Side 5	100.3
Thickness at	55	relative humidity for	Side 4	99.9
Thickness at	55	relative humidity for	Side 5	100.3
Thickness at	75	relative humidity for	Side 5	100.9

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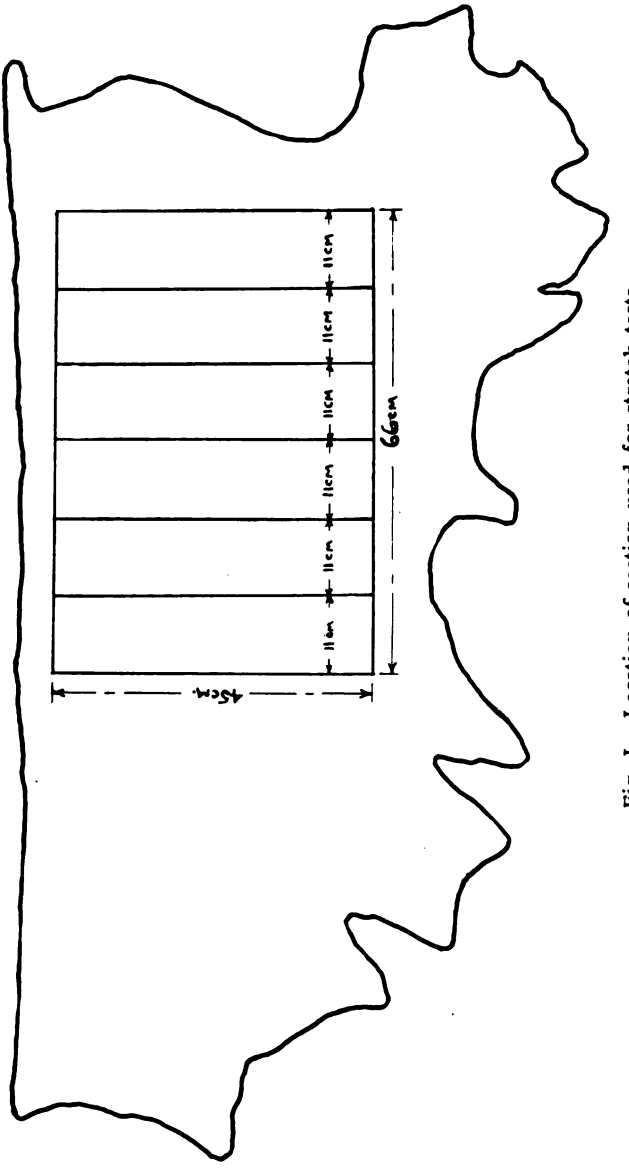

Fig. 1.—Location of section used for stretch tests
Each 11 x 45 cm. strip was laid off into 30 test blocks, 11 x 1.5 cm., parallel to the back bone line.

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All test pieces from the three sides were placed on end in individual meshes of open wire racks, so as to be completely exposed, and were put in the humidity room after it had been adjusted to 70° F. and 35 per cent R. H. Throughout these experiments the temperature of the room was kept constant at 70° F. and the humidity was changed as shown. None of the pieces were removed from the room until they had been tested, and the experiments at the different conditions were completed in an uninterrupted sequence of days.

In order to follow the conditioning of the test pieces, every tenth one was weighed every day until the last two weights were constant. The weights generally agreed within 1 to 2 mg. and rarely differed by more than 3 mg., or a variation at the most of from 0.10 to 0.15 per cent on the weight of the test pieces. When conditioned to constant weight the test pieces were treated as outlined below:

Side 3—*Every* test piece broken at *70° F.—35 per cent R. H.*

Side 4—*Every* test piece weighed at *70° F.—35 per cent R. H.* and *alternate* strips tested at this condition. *Remaining* test pieces weighed at *70° F.—55 per cent R. H.* and tested at this condition.

Side 5—*Every* test piece weighed at *70° F.—35 per cent R. H.* and alternate strips tested at this condition. *Remaining* test pieces weighed at *70° F.—55 per cent R. H.* then at *70° F.—75 per cent R. H.* and broken at last condition.

Strength and Stretch Results: Figures 2, 3, and 4 show the individual data for each section. The results in Figure 2 particularly show the lack of uniformity in the physical properties of a piece of leather, especially when it is recalled that the section represents but a rather restricted area of the side. This fact is, of course, well known, although often not fully appreciated. Data like those given in Figure 2 emphasize the necessity for a large number of results from strictly comparable tests before any sound conclusions can be drawn. Even in these experiments in which adjacent test pieces were removed from one another by only 1 cm., numerous instances can be found in which the difference in strength between two such adjacent strips is material.

The section from Side 3 was used as a control for the plan of the experiments. After breaking every piece of this section at

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←Toward Head — Backbone Line — Toward Tail→

66 CM.

45 CM.

35-	35-163-19	35-174-25	35-190-29	35-161-17	35-230-24
35-194-20	35-138-20	35-170-25	35-204-31	35-174-19	35-185-25
35-188-25	35-144-22	35-164-24	35-185-22	35-186-20	35-166-20
35-148-22	35-144-22	35-147-22	35-170-22	35-184-20	35-156-20
35-156-24	35-139-22	35-166-25	35-172-27	35-168-17	35-147-32
35-158-25	35-142-34	35-170-27	35-174-34	35-160-20	35-141-42
35-167-25	35-122-32	35-154-27	35-147-34	35-150-29	35-138-34
35-169-27	35-121-37	35-141-36	35-159-36	35-145-29	35-109-39
35-166-39	35-122-41	35-135-34	35-150-41	35-138-42	35- 98-36
35-162-27	35-122-42	35-125-34	35-151-39	35-129-42	35- 97-39
35-176-42	35-128-42	35-136-34	35-149-37	35-123-47	35- 86-36
35-167-25	35-134-41	35-141-37	35-130-32	35-116-47	35- 86-36
35-157-42	35-154-44	35-140-34	35-136-39	35-116-39	35- 93-34
35-174-44	35-139-41	35-134-41	35-144-49	35-118-47	35- 95-31
35-171-41	35-141-41	35-128-31	35-140-34	35-114-44	35-108-34
35-158-34	35-142-42	35-130-32	35-128-36	35-118-37	35-107-31
35-160-36	35-154-41	35-122-29	35-136-34	35-119-32	35-108-29
35-167-39	35-161-36	35-131-27	35-124-34	35-119-27	35-116-27
35-160-36	35-163-41	35-135-29	35-132-41	35-119-25	35-118-24
35-157-36	35-161-41	35-136-29	35-139-36	35-121-24	35-130-25
35-160-34	35-156-36	35-142-39	35-156-39	35-127-20	35-145-22
35-174-34	35-146-34	35-161-36	35-159-36	35-140-17	35-137-22
35-176-37	35-167-32	35-159-32	35-150-25	35-149-20	35-139-22
35-171-36	35-169-32	35-155-29	35-162-32	35-167-22	35-126-22
35-172-34	35-173-31	35-156-31	35-162-29	35-147-20	35-146-25
35-214-39	35-201-31	35-153-29	35-163-34	35-141-20	35-140-27
35-213-34	35-208-29	35-195-31	35-163-31	35-151-24	35-141-25
35-216-34	35-224-31	35-198-25	35-156-27	35-140-25	35-130-22
35-206-31	35-247-31	35-262-31	35-148-25	35-174-29	35-152-31
35-187-31	35-237-31	35-305-32	35-220-29	35-193-22	35-161-25

Avg. A.—(Odd) 173-34	(Even) 159-34	(Odd) 158-30	(Even) 159-34	(Odd) 143-28	(Even) 128-29
Avg. B.—(Even) 174-32	(Odd) 159-34	(Even) 160-31	(Odd) 154-33	(Even) 144-28	(Odd) 134-29

Mean of Avg. A.—153-32

Mean of Avg. B.—154-31

In test blocks: 1st figure = Percentage relative humidity; 2nd figure = Break in kgs. per sq. cm.; 3rd figure = Percentage stretch.

In averages: 1st figure = Break in kgs. per sq. cm.; 2nd figure = Percentage stretch

After adjusting room at 35 per cent R. H. test pieces were conditioned 66 hrs. before starting to test. During conditioning:—temp. 69°-70.5° F. : R. H. 34 per cent-37 per cent

Figure 2.—Section from Side 3

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←—— Toward Head		Backbone Line		Toward Tail ——→	
←——		66 CM.			——→
35-169-19	55-265-25	35-260-29	55-237-32	35-172-24	55-219-25
55-187-32	35-220-22	55-267-29	35-204-22	55-169-25	35-168-20
35-171-31	55-206-20	35-245-20	55-230-30	35-123-20	55-156-25
55-157-27	35-181-20	55-239-34	35-195-24	55-173-29	35-142-25
35-172-29	55-206-27	35-172-24	55-214-37	35-148-24	55-149-31
55-177-36	35-168-22	55-220-36	35-174-25	55-169-29	35-137-31
35-155-34	55-201-34	35-204-34	55-198-36	35-134-24	55-144-36
55-138-24	35-178-39	55-230-39	35-172-25	55-163-32	35-112-31
35-150-37	55-197-42	35-197-36	55-188-34	35-151-32	55-133-54
55-173-44	35-174-41	55-214-41	35-131-25	55-161-39	35-100-39
35-151-41	55-195-41	35-166-31	55-157-34	35-127-34	55-110-50
55-169-42	35-166-39	55-178-37	35-134-31	55-143-49	35- 87-47
35-148-42	55-176-39	35-150-37	55-154-36	35-129-46	55-102-49
55-163-44	35-155-36	55-177-46	35-134-34	55-149-53	35- 91-42
35-134-39	55-188-44	35-129-34	55-164-42	35-111-36	55-113-47
55-161-41	35-180-41	55-162-39	35-152-42	55-146-56	35-100-41
35-132-39	55-195-41	35-134-32	55-156-42	35-118-37	55-122-46
55-146-41	35-173-41	55-158-37	35-143-31	55-135-56	35-108-36
35-148-41	55-191-42	35-143-29	55-162-44	35-108-36	55-124-42
55-181-41	35-171-37	55-153-31	35-129-39	55-126-39	35-106-36
35-181-37	55-190-39	35-128-27	55-134-36	35- 95-24	55-135-39
55-214-41	35-174-37	55-140-32	35-123-34	55-137-37	35-118-31
35-174-36	55-188-36	35-148-36	55-121-34	35-126-29	55-138-32
55-204-36	35-175-34	55-158-34	35-116-32	55-142-36	35-133-34
35-190-34	55-179-34	35-148-39	55-129-31	35-127-29	55-170-39
55-215-36	35-198-37	55-148-34	35-134-29	55-141-29	35-153-31
35-179-32	55-231-37	35-156-23	55-140-29	35-126-25	55-185-37
55-221-36	35-197-31	55-206-34	35-154-25	55-150-32	35-163-32
35-216-27	55-240-36	35-205-31	55-204-25	35-125-20	55-186-37
55-270-32	35-244-31	55-261-32	35-232-22	55-177-29	35-166-29
Avg. at 35% R. H.—165-35	184-31	172-34	155-29	128-29	126-34
Avg. at 55% R. H.—185-37	203-36	194-36	172-35	152-38	146-39

15 CM.

Avg. of all at 35 per cent R. H.—155-32.
Avg. of all at 55 per cent R. H.—175-37.

In test blocks: 1st figure = percentage relative humidity: 2nd figure = break in kgs. per sq. cm.: 3rd figure = percentage stretch.
In average: 1st figure = break in kgs. per sq. cm.: 2nd figure = percentage stretch.
After adjusting room at 55 per cent R. H. test pieces were conditioned 45 hrs. before starting to test. During conditioning:—Temp. 69°-71° F.: R. H. 54 per cent to 56 per cent.

Figure 3.—Section from Side 4.

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←Toward Head		Backbone Line		Toward Tail→	
← 66 CM. →					
35-208-22	75-339-32	35-299-19	75-343-31	35-156-17	75-297-31
75-264-31	35-210-20	75-319-31	35-252-19	75-231-32	35-199-15
35-210-17	75-275-34	35-200-20	75-309-34	35-181-24	75-269-34
75-267-32	35-178-24	75-291-31	35-210-19	75-251-36	35-156-20
35-195-20	75-267-36	35-184-17	75-276-37	35-180-24	75-228-32
75-266-34	35-170-24	75-293-34	35-211-22	75-229-36	35-128-19
35-184-25	75-269-36	35-170-17	75-272-37	35-162-25	75-202-41
75-290-41	35-176-19	75-276-37	35-175-17	75-241-37	35-116-24
35-195-32	75-272-39	35-173-20	75-280-39	35-161-24	75-175-41
75-282-42	35-180-19	75-256-36	35-157-24	75-226-41	35-100-24
35-199-25	75-268-42	35-159-27	75-256-36	35-149-19	75-164-46
75-272-42	35-169-20	75-229-39	35-168-31	75-205-41	35-101-29
35-192-24	75-262-41	35-148-29	75-255-37	35-142-27	75-176-42
75-258-39	35-165-29	75-243-44	35-169-24	75-217-41	35-111-31
35-177-32	75-255-41	35-154-27	75-263-36	35-149-27	75-194-39
75-246-44	35-192-25	75-251-42	35-178-24	75-220-39	35-120-25
35-199-25	75-259-44	35-175-31	75-289-37	35-146-24	75-191-37
75-270-46	35-175-31	75-284-41	35-183-20	75-205-34	35-118-22
35-200-25	75-256-42	35-190-31	75-264-37	35-163-19	75-210-36
75-260-42	35-190-19	75-271-37	35-163-22	75-206-34	35-135-24
35-200-34	75-251-37	35-179-27	75-236-37	35-143-24	75-232-39
75-221-39	35-185-31	75-234-36	35-164-19	75-197-34	35-161-27
35-193-34	75-292-37	35-195-25	75-223-36	35-140-22	75-219-39
75-232-41	35-222-31	75-273-34	35-185-31	75-210-36	35-163-24
35-223-24	75-302-36	35-243-27	75-292-41	35-156-20	75-229-42
75-273-42	35-247-24	75-323-37	35-260-32	75-269-36	35-170-31
35-243-24	75-317-36	35-268-31	75-350-37	35-203-29	75-237-42
75-281-39	35-243-29	75-340-37	35-261-25	75-296-27	35-158-29
35-200-34	75-329-36	35-268-25	75-231-31	35-176-17	75-245-44
75-262-46	35-200-22	75-321-31	35-238-20	75-311-27	35-196-24
Avg. at 35% R. H.—201-27	193-25	200-25	198-23	160-23	142-25
Avg. at 75% R. H.—263-40	281-33	280-37	276-36	234-35	218-39

45 CM.

Avg. of all at 35 per cent R. H.—182-25.
Avg. of all at 75 per cent R. H.—259-38.

In test blocks: 1st figure = percentage relative humidity: 2nd figure = break in kgs. per sq. cm.: 3rd figure = percentage stretch.
In average: 1st figure = break in kgs. per sq. cm.: 2nd figure = percentage stretch.
After adjusting room at 75 per cent R. H. test pieces were conditioned 50 hrs. before starting to test. During conditioning:—Temp. 68.5°-70.5° F.: R. H. 72 per cent to 77 per cent.

Figure 4.—Section from Side 5.

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35 per cent R. H. the results were averaged according to the same system used for the other two sections. It will be noted that the two averages thus obtained for the section from Side 3 are almost identical.

Immediately under each section charted in Figures 2, 3 and 4 are given the average break load in kgs. per sq. cm. and the average percentage stretch or elongation of the test pieces for each 11 by 45 cm. strip. Below this are given the averages for the entire section at the respective testing conditions. These data and some additional results have been charted in Figures 5, 6, 7 and 8, the values for the strips being connected to aid in readily visualizing them.

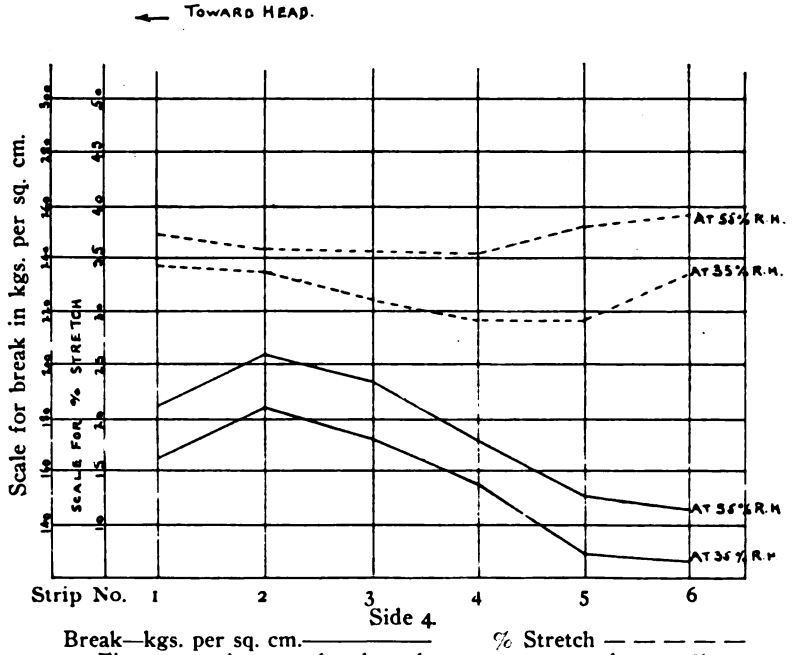

Figure 5: Average break and percentage stretch at 35% and 55% R. H. for 6 strips from Side 4.

Discussion of Results: The results convincingly prove the conclusion previously drawn from less extensive and accurate data that relative humidity conditions will have a decided effect on the physical properties of leather, certainly of the type used in these experiments. This is strikingly shown by Figures 5 and

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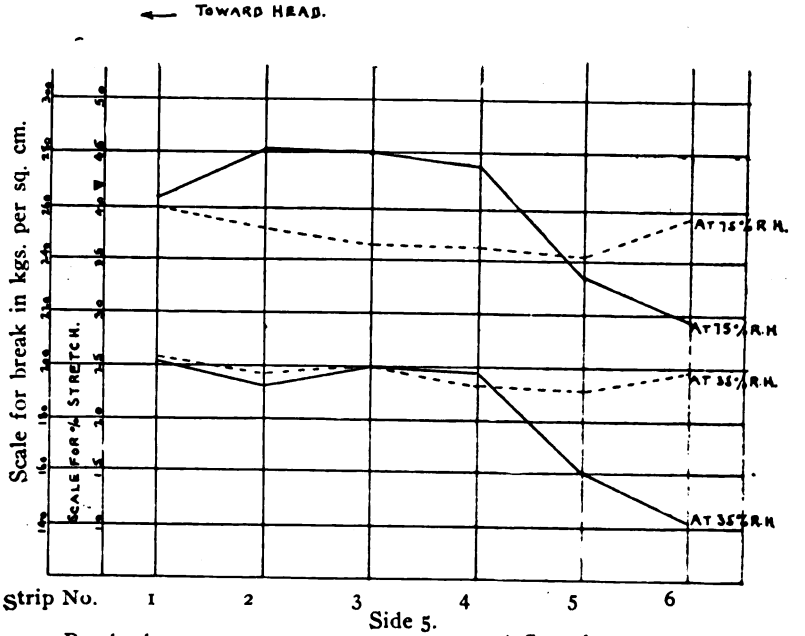
6. It will also be noticed that the values for both Sides 4 and 5 have the same trend, and the actual increases in break load per



Break—kgs. per sq. cm.———— % Stretch — — — — —

Figure 6: Average break and percentage stretch at 35% and 75% R. H. for 6 strips from Side 5.

sq. cm. and in per cent stretch, based on the average value for each strip of each section, are remarkably and indeed surprisingly uniform across the section. These same results have been expressed in Figure 7 as percentage increase, calculated on the results obtained at 70° F—35 per cent R. H.

For an increase of 20 per cent relative humidity, from 35 per cent to 55 per cent, the average increase for the entire section was 12.9 per cent in tensile strength and 15.7 per cent in stretch or elongation. For an increase of 40 per cent relative humidity, from 35 per cent to 75 per cent, the average increase in tensile strength was 42.3 per cent and in stretch or elongation it was 53.1 per cent. It will be noted from this that the increase in strength is not directly proportional to the increase in relative humidity but would seem to be directly related to the moisture content of the leather. While this can not be positively concluded

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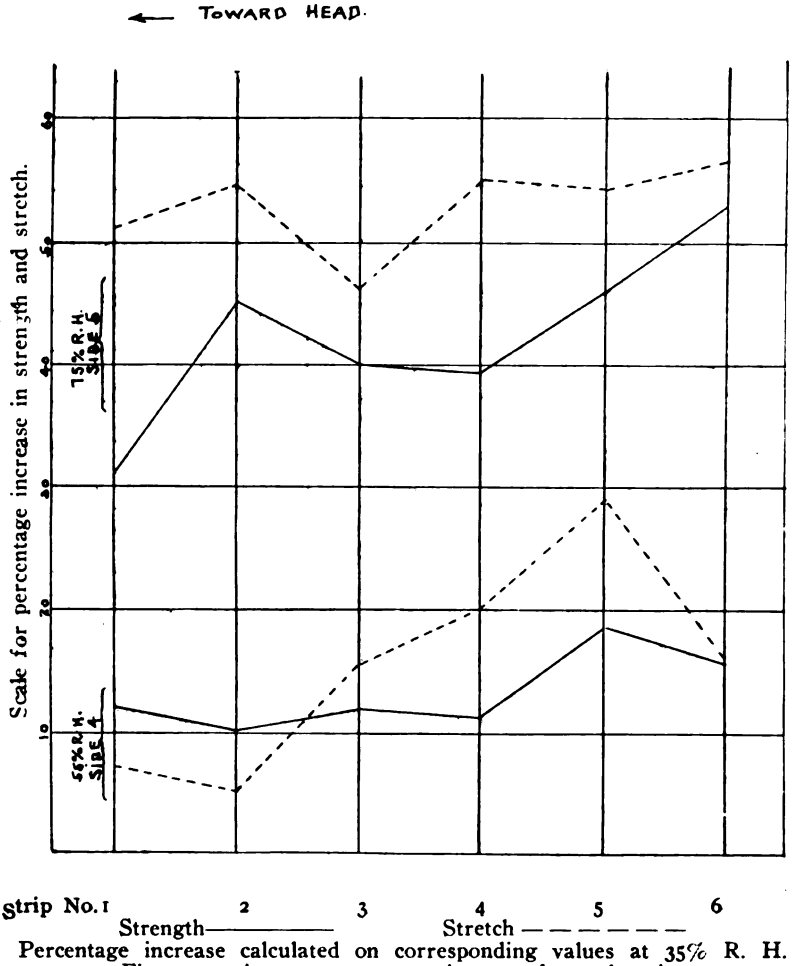
from these experiments, because the results at 55 per cent and at 75 per cent relative humidity were obtained from different sides, the evidence that such is the case is indeed nearly convincing, as will be realized upon comparing the values given in



Percentage increase calculated on corresponding values at 35% R. H.
Figure 7: Average percentage increase for each strip at right angle to backbone line.

Figure 8 for strength, stretch, and moisture, bearing in mind the fact that the sides were from the same class of skins tanned in the same manner by one tanner. It will be seen from this figure that the percentage gain in moisture, as determined by

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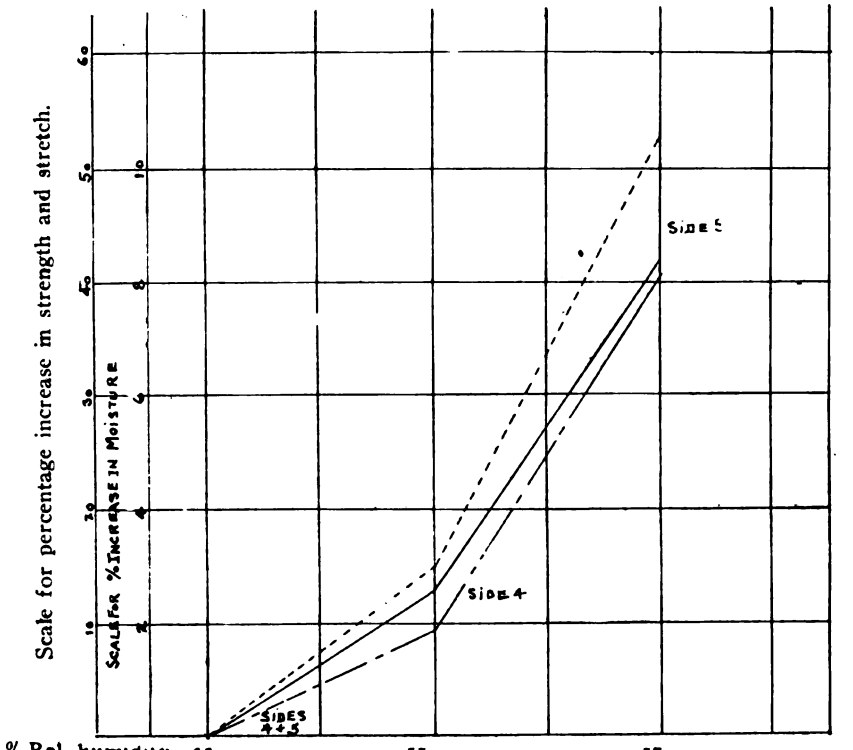
weighing and by calculating on weight at 35 per cent relative humidity, is 1.9 at 55 per cent relative humidity and 8.2 at 75 per cent relative humidity, or also practically four times as much at 75 per cent relative humidity as at 55 per cent. Furthermore, the gain in weight or moisture for both Side 4 and Side 5 checked very closely at 55 per cent relative humidity, the average percentage gain being 1.89 and 1.95, respectively. This would



Percentage increase calculated on corresponding values at 35% R. H.

Figure 8: Average percentage increase for entire section from Sides 4 and 5.

indicate that the two skins had the same moisture absorption "coefficient," so to speak, and that therefore the absorption of moisture and, in turn, the increase in strength and stretch are not directly proportional to the increase in relative humidity. This confirms Rudeloff's findings and also Roys' conclusion that

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the effect of a change in the relative humidity is greater at high than at low humidities.

Conclusions

These experiments were planned to show possibly the maximum effect of humidity on vegetable-tanned leather. With this object in mind, lightly tanned, unloaded and unstuffed leather was used. The results for such leather show a marked effect, entirely too great to be ignored in testing work. Of course, the actual percentage values found in these experiments can not be accepted for other leathers, because of the numerous variables and factors in leather making. There can be little doubt, however, that humidity exerts an influence upon all kinds of leather, the effect differing only in magnitude. It would seem reasonable to assume that the effect would be least for heavily oiled or greased leathers and probably greatest for lightly tanned hides and skins and for leathers containing hygroscopic materials. The value of these results lies in redirecting attention to and in emphasizing the importance, or better, the absolute necessity of testing under humidity control and then only after the test pieces have been thoroughly conditioned or have reached complete equilibrium with the moisture at the testing conditions. Especially is this true for certain types of fundamental investigational work, such, for example, as the determination of strength and stretch in different positions of the hide; or particularly the comparison of the physical properties of unoiled or unstuffed leathers with those of the corresponding oiled or stuffed pieces; or a comparison of different belting leathers. Considerable work of this or similar nature has been and is being done. Its accuracy and value would seem to be in question in view of the data given and discussed in this paper.

In the course of this and other work by the Bureau on humidity, several interesting and possibly important questions have arisen. It is planned to obtain data upon these. So far, from the results given here, it is evident that humidity control conditioning is essential, but it may prove necessary to go even further than

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this and "pre-condition" the leather, so to speak, before exposing and testing it at a given relative humidity.

LEATHER AND PAPER LABORATORY,
BUREAU OF CHEMISTRY, WASHINGTON. D. C.

DISCUSSION

A. C. ORTHMANN: I would like to ask whether the leather was properly stuffed and filled with oils and greases. The variation is so great that it seems almost impossible.

R. W. FREY: The leather was not oiled or stuffed, being in the "crust" condition. I am inclined to think that the effect of humidity would not be as great with heavily oiled leathers. Of course we could not include all types of leather at this time and our idea was to get the maximum effect—the type of leather which it would seem reasonable to suppose would give the maximum effect; and the next step is to get leather to give the minimum effect. The idea here was to see the effect which would be produced under rather ideal absorption conditions.

F. P. VEITCH: I would like to emphasize even more strongly than Mr. Frey has, perhaps, since it is so important to the tanner, how great the effect of humidity is, and how useless, in my judgement, it is to make a strength test to-day, and next week on another piece, knowing nothing whatever about the humidity or the moisture content and try to draw conclusions from them.

Under certain conditions the best leather would give the poorest results. This work was done to drive home the effect of humidity in everyday work. Unless humidity is controlled the results of strength test in leather are absolutely useless.

On the question of greased leather, I am inclined to agree with Mr. Frey's statement, but on the other hand, I expect that the time of reaching equilibrium with greased leathers would be greatly prolonged, after which perhaps the effect of humidity would be quite as great.

G. W. SCHULTZ: I would like to ask if the effect attributed to relative humidity is due to the increase in moisture content in the leather.

F. P. VEITCH: Entirely to that, probably.

G. W. SCHULTZ: Then anything which changes the moisture content of leather should have its resulting effect on the stretch and strength of the leather.

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F. P. VEITCH: I think so.

F. M. LOVELAND: I would like to say, in regard to the last question, that the same effect holds good in sole leather. I have seen it worked out. For instance, in shutting down a tannery, I had the experience one time that the rolling lofts ceased work, and instead of working the leather out of the loft, as would naturally have resulted, the leather was allowed to stay within the lofts. Now the same finishing conditions were in effect, the leather was handled the same way before it went into the loft and the same way after it went out of the loft, but it was very brittle and cracky. It was necessary to oil it heavily on rolling to take that out.

Then the tannery was started again, with the same amount of oil, same mixture, everthing identical, except that a shorter time for drying took place, and that leather was all right. It was simply a moisture condition. And the leather, even after dipping, after the samming process, takes on the moisture very slow. You can dip it in warm water, treat it just the same, and you will find that your leather stays brittle and hard.

PRESIDENT SMALL: This once more emphasizes the absolute necessity of a complete knowledge of what one is doing if he is going to secure results that are of any value to him. Last year we tried to emphasize that same point in connection with the matter of sampling—the absolute necessity of taking a sample that is known, that we know what part of the hide it comes from. We find here that it is necessary to know as well definitely what percentage of moisture there is in our leather, if the results we are going to get are going to be really informative.

PROGRESS IN THE PHYSICAL CHEMISTRY OF GELATIN*

By C. R. Smith

BUREAU OF CHEMISTRY, U. S. DEPARTMENT OF AGRICULTURE,
WASHINGTON, D. C.

Colloid chemistry dates its origin to the studies of Thomas Graham upon the differences in diffusibility and ability to crystallize of substances which Graham classed as "different worlds of matter." Gelatin or glue was selected as typical of the slowly

* Read at the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Ontario, Canada, June 22, 1922. Published by permission of the Secretary of Agriculture.

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diffusible, non-crystallizing forms of matter and the Greek word kolla, meaning glue, was selected to designate this class of substances, commonly referred to as colloids.

In spite of the prominent position thus held by gelatin in colloid chemistry and its importance as a commercial product, the information to be gained from the literature and textbooks is indeed inaccurate and confusing. Working with an indefinite product of varying jelly strength and ash content, it is not surprising to find few reliable measurements of its physical and chemical properties. During the last few years, however, we note a renewed interest in gelatin research which promises to yield the necessary foundation for real growth. Gelatin of the highest possible jelly strength, showing a mutarotation ratio of 2.2, is being manufactured. This gelatin can be freed from ash[1] by laboratory methods, giving material of standard quality. While we are, perhaps, not yet dealing with a 100 per cent pure protein, this material is satisfactory for most experimentation. The writer has paid much attention to possible methods for fractionation and crystallization but without success. The method of von Weimarn[2] for crystallizing gelatin, involving the gradual withdrawal of water from aqueous alcholic solution of gelatin at 60-70° C. by means of potassium carbonate, has failed in his hands. Recently Bradford, in the *Biochemical Journal*, claimed to have obtained gelatin crystals. It is possible that the conditions were such as to produce insoluble iso-electric gelatin. It appears that we have not yet found a means to crystallize gelatin to the point of giving us a ready supply of the 100 per cent purified article. It is unfortunate that so much work has been done with ash containing gelatin. Studies in osmotic pressure and precipita-

[1] Patent application, Serial No. 390,253 dated June 19, 1920 for the preparation of ash free gelatin was made by the author. Dr. Loeb, in his book on "Proteins and the Theory of Colloidal Behavior" and elsewhere has erroneously credited Miss Field, publishing in *J. A. C. S.*, March, 1921, as the discoverer of ash free gelatin. The author, in addition to his prior application for a public service patent, also verbally communicated to Mr. J. A. Wilson in the early part of 1920, that he had produced ash free gelatin and was studying its properties. There was evidently a race made in vain by Miss Field in her "preliminary" paper to antedate the author's right of discovery.

[2] *Grundzüge d Dispersoid Chemie*, 1911, p. 106.

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tion, and, to a smaller extent perhaps, swelling experiments are of doubtful value when performed with such gelatin.

To illustrate the significance of ash in gelatin I shall take this opportunity to state the results of a few interesting experiments in preparing silver bromide emulsions for photography with ashless gelatin. An emulsion of silver bromide is made by precipitating silver nitrate with potassium bromide in the presence of ashless gelatin and allowed to jelly, and the excess of bromide is washed out. The emulsion, which is perfectly transparent during this treatment, can now be "cooked" indefinitely without ripening. These experiments show that the ripening process in commercial plate making is largely effected by the ash constituents of the gelatin. Let me suggest to photographic chemists that research might be profitably directed to studying the effect of added electrolytes on the ripening of emulsions in ashless gelatin. Ash free gelatin can be prepared by washing powdered gelatin with acidified sodium chloride solutions and pure water according to the writer's published method. It is to be noted that this replacement of calcium salts by sodium salts in proteins and other colloids, such as agar and pectin, is a general reaction. The uncombined calcium salts diffuse out without difficulty, although the last traces of acid are difficult to remove.

Ash free gelatin looks like the ordinary kind but if we prepare a 1 per cent jelly it soon takes on the appearance of "smokiness," increasing in intensity until flocculation occurs.

Ash free gelatin is an unnecessary refinement for table gelatin where a clear jelly is demanded, but it is very necessary in studying certain of its physico-chemical properties.

Let us now review in general terms the newer knowledge of gelatin and its properties. We will consider briefly the following divisions of this subject:

1. Jellying and liquefaction.
2. Amphoteric properties.
3. Osmotic pressure.
4. Swelling.

Jellying and Liquefaction. Jellying and liquefaction of gelatin are best studied by means of the polariscope, supplemented by other physical tests. It has been shown that gelatin of the highest quality approximates a definite standard of jellying power which is

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expressed in polariscopic units by saying that the mutarotation ratio[3] is 2.2, with a possibility that further refinement will lead to a slightly higher figure. This gelatin just produces a jelly at a concentration of 0.55 g. per 100 cc. at 15° C. if cooled a sufficient length of time.

Mutarotation is a familiar word in sugar chemistry. Glucose has been shown to exist in the alpha, beta and gamma forms, for it gives three widely different values of specific rotation under different conditions and the solid forms have been isolated. The mutarotation results indicate two forms of gelatin in jelly and liquid form and possibly a third in the dry form. The liquid or sol form exists above 35° C., while the gel form is stable below 15° C. Between these temperatures an equilibrium exists. The effect of salts and acids on the mutarotation and the jelly strength has been extensively studied. It has long been known that sulfates raise the melting point while bromides and iodides lower it. All of this is clearly reflected in the polariscopic readings. It should be understood that the effect of salts and weak acids is to cause an equilibrium shift which is equivalent to a raising or lowering of the temperature. For example, potassium iodide lowers the melting point, tending to produce more of the sol form. If we cool the gelatin, say to 5° C., we develop the fullest jelly strength possible if we wait a sufficient length of time.

Amphoteric Properties. The results of all recent work point to the combination of acids and bases with gelatin. Further, it has been shown that this union is stoichometric in character, such as would be expected in any amphoteric body. If we choose to use the term adsorption, it must be supposed that the adsorption is specific for hydrogen or hydroxyl ions in dealing with acids and bases and we are justified either by reason of correctness or convenience in referring to gelatin chloride, sodium gelatinate, etc.

When gelatin is immersed in univalent acids or polyvalent acids ionizing as univalent, it combines with equivalent amounts at the same hydrogen ion concentration. Using a bivalent acid, we get a somewhat greater combination which appears to be due to the diminished swelling. Similar conclusions hold for univalent and bivalent bases.

[3] C. R. Smith, *J. A. C. S.*, 43, p. 1350 (1921).

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Osmotic Pressure. The results obtained in this study will eventually prove of the greatest value in formulating a correct theory of swelling and will give us the best insight into the mechanism of the reactions of ions and gelatin. Beyond the shadow of a doubt we are dealing with ionic phenomena in agreement with the general results of the newer physical chemistry. The osmotic pressure results can be duplicated with considerable accuracy and will lend themselves to mathematical treatment. They are of diverse character but unquestionably show that valency of ions and mass relations are influencing the results.

Because of the interdependence of osmotic pressure and swelling, the principal results of the former will be discussed under "Swelling." It should be pointed out that the maximum of osmotic pressures obtained with univalent acids is nearly the same as that for univalent bases; likewise the pressures from bivalent bases and acids are nearly equal. This may be only coincidence but should not be disregarded.

Swelling. It is generally agreed that swelling is the result of osmotic forces within the jelly. Under conditions which dispose to the highest osmotic pressure as found in the collodion membrane, the greatest swelling is produced in the jelly. The maximum osmotic pressure of 0.5 per cent melted gelatin surrounded by dilute acids occurs at a normality of 0.001, while the maximum of a 2.0 per cent melted gelatin or jelly is at 0.004 normal.

The most important phenomena which should be explained in a theory of swelling are the following:

(1) The phenomena observed in the osmotic pressure of gelatin solutions which include—

(a) The equivalence of univalent ionizing acids,
(b) The equivalence of univalent ionizing bases,
(c) The equivalence of bivalent ionizing acids,
(d) The equivalence of bivalent ionizing bases,
(e) The very much lower osmosis with bivalent acids and bases compared to univalent ones.
(f) The effect of salts which show that osmosis is limited to the salt ions which carry electrical charges opposite to those of the gelatin.

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(2) The relation of osmosis to swelling which includes—

(a) A comparison of relative maximum, minimum, and intermediate values,

(b) A comparison of alkaline and acid osmosis and swelling.

(3) The distribution of acids, bases, and salts between water and gelatin.

The most scientific attempt at a theory of swelling has been made by Procter, whose work was extended by Procter and Wilson, and by Wilson and Wilson. These workers made use of the conclusions reached by Donnan and coworkers in explaining certain membrane equilibria results. The application to gelatin swelling consisted in the assumption that acid and salt electrolytes would distribute themselves unequally between jelly layer and water layer because of the presence within the jelly of ions attached to nondiffusible gelatin molecules or particles. The degree of swelling is conditioned by the excess of diffusible ions in the jelly over those in the water layer (an excess will necessarily be present).

The fundamental equations in this theory are:

$$(1)\quad x^2 = y(y + z)$$

$$(2)\quad e = 2y + z - 2x$$

$$(3)\quad e = -2x + \sqrt{4x^2 + z^2}$$

when a binary electrolyte, such as hydrochloric acid, is used which will combine with the gelatin. It is easy to show that when two binary electrolytes are used, such as a mixture of sodium chloride and hydrochloric acid in which only the acid is supposed to combine with the gelatin, we have

$$(4)\quad (x + x')^2 = (y + y')^2 + (y + y')\,z$$

$$(5)\quad e = 2(y + y') + z - 2(x + x')$$

$$(6)\quad e = -2(x + x') + \sqrt{4(x + x')^2 + z^2}$$

In the equations above, x refers to the concentration of the H or Cl ion of the HCl, and x′ refers to the Na ion of the NaCl, both of which are contained in the water, while y and y′ refer to the respective concentrations in the jelly and z refers to the concentration of gelatin chloride. When $x' = O$, then $y' = O$ (when no NaCl is used) and equations (4), (5), and (6) become identical with (1), (2), and (3).

From the foregoing deductions we are to expect that while salt does not distribute unequally between water and gelatin alone,

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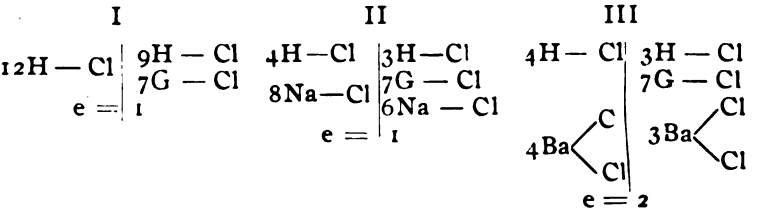
when acid or alkali is present in addition to the salt, we should find an excess of salt in the water layer. No experiments have been offered to prove that this takes place. My own experiments have shown that little or no excess is present in the water. I think, however, that these should be repeated.

Procter and Wilson[4] proved that the internal acid of the jelly was less than in the water by adding solid salt to shrink the jelly. The extruded salt solution was titrated and compared with the external acid. They assumed that salt did not cause increased combination of gelatin with the acid.

Loeb considers that the distribution takes place according to Donnan's theory. He has made measurements of the potential difference existing between external and internal acid by the Compton electrometer and concludes that the theory was verified. It will be noted that Loeb places the unequal distribution of ions (or the Procter and Wilson *e*) at the surface of the collodion membrane and attempts to show the correctness of the Donnan equilibrium equations. Procter and Wilson previously had considered *e* of melted gelatin to exist at the molecules or particles.

Let us consider the results to be expected on the basis of Donnan's theory as applied by Loeb[5] to gelatin osmosis in the presence of hydrochloric acid with sodium or barium chloride. My results showed that barium chloride and sodium chloride of the same normality with respect to the chlorine ions had the same effect in hydrochloric acid osmosis. This has been recently confirmed by Loeb who, however, maintains that this was to be expected on the basis of Donnan's theory. With this conclusion I cannot agree.

Consider the following distributions:



In both I and II all ion products are satisfied and $e = 1$. Now consider that the external 4 $BaCl_2$ in III is fixed equivalent to

[4] *J. Chem. Soc.*, 109, 307 (1916).

[5] Loeb's studies on gelatin have been published in book form with the title "Proteins and the Theory of Colloidal Behavior," by McGraw-Hill Book Co.

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8 NaCl with respect to the chlorine ion in the external water. If we assume an equivalent distribution in the jelly we get a value of $e = 2$. If we object to this distribution in the jelly but demand that

$$\text{(external)} \quad \frac{BaCl_2}{(HCl)^2} = \frac{BaCl_2}{(HCl)^2} \quad \text{(internal)}$$

a different distribution for both $BaCl_2$ and HCl is required to maintain the value of e. We are thus led into a complex set of distributions when the simple fact may be that the chlorine ion concentration is equal in the jelly phase of II and III and the barium ion is without any effect whatever.

If we are to apply Donnan's theory to the swelling of gelatin we need some accurate measurements of the distribution of salts and acids between water and jelly (or contents of a collodion membrane). The theory is certainly flexible enough to fit many facts in a qualitative way at least, but we are now ready for a rigid quantitative agreement. Less attention should be paid to theories of agglomeration, hydration, etc., and more attention given to accurate quantitative and reproducible measurements such as are demanded by Donnan's theory.

Procter and Wilson in their theory of gelatin swelling balanced the osmotic forces of the jelly against its elasticity which was considered to follow Hooke's law in that the greater the swelling the greater the opposing force. A swollen jelly could be compared to a blown-up balloon. I am of the opinion that the analogy would be more nearly correct if it were assumed that the balloon was covered with small holes and a constant pressure was maintained. As the pressure increases the balloon stretches and the leakage is greater. There is positive evidence that a "maximum" swollen gelatin shows considerable pressure when the leaks are stopped by enclosing it in a collodion membrane. This leakage is probably very great in swelling with univalent alkalies where the osmotic pressure is equal to or greater than that in acids, but the swelling is only a little more than half as much as with univalent acids.

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A LAYMAN IN RESEARCH *

By F. M. Moffat

If I am somewhat halting in my remarks, either as a layman in research, or in bringing the greetings of the Tanners' Council, I trust it may be understood and explained that I have absorbed so many technical phrases during the last twenty-four hours that my English may come a little haltingly, and may have to be translated.

I shall speak briefly, and I trust to the point, particularly in bringing you the greetings of the Tanners' Council. I regret that neither Mr. Thayer nor Mr. Robertson could have been here. There were many reasons why they were delayed, but their greetings, as they have often expressed them to me and the other members of the Council, are none the less hearty.

I suppose at no time in the history of our great trade do the members of that organization feel a greater sense of dependency upon you men, who are delving into the problems that confront you, than they do at this time. You all know the history of the last two or three years and now we, on our side, (and when I speak of "we" I mean the men who have the economic side) are facing the reconstruction period, and we have all of a sudden discovered that we have a very strong ally in you men of the American Leather Chemists' Association.

In a brief conversation with Mr. Small last evening, I tried to demonstrate to him how fine a function had been his during his presidency of your Association. The results of that cannot be judged by saying that there are very few tanners here at Bigwin to-day. The results must be judged by what has happened.

You men have put yourselves solidly behind the proposition that there is a highly scientific turn to our business, and with your support we have gone ahead; and the message that I would bring from the Tanners' Council to-day is that with your support we have effectually done what I regard as one of the finest pieces of constructive work that has ever been perfomed by any trade organization in this country, and I say it with great appreciation of the words which I am using.

* Address to the 19th Annual Meeting of the A. L. C. A., at Bigwin Inn, Ontario, Canada, June 22, 1922.

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If you will point out to me an association of men who have taken business more seriously than we have in the last two years, in spite of everything that has been said against us, in spite of having been called to the bar of justice and called robbers and profiteers, I should like to see it. We have taken the thing broadly, and we have gone honestly and deliberately to science and said "if we are all that, show us our mistake; we are perfectly ready," and we have asked you scientific men to back our effort and you have done it finely, nobly and broad-mindedly, and that, Gentlemen, I think Mr. Small may reckon as some of the results of his presidency.

That is the message I would bring from the Tanners' Council. You need no authority or written word. You know in your own hearts what you have done, and if the shoe fits put it on.

I am minded of the old Scotch woman, who listened to the new parson, and after church was over loitered carefully so that she might be overtaken, and have a word with him. It happened as she planned, and the conversation ran about as follows:

"Well, Mrs. MacIntosh, what did ye think of the sermon? A moment's pause and the glint of battle was in Mrs. MacIntosh's eye: "I didna think weel of it; in the first place, ye read it. In the second place, ye didna read it weel; in the third place it wasna worth the readin."

It may well be that I must plead guilty to all these counts, but at any rate, layman and parson alike must sometimes be listened to, and if I, layman that I am, am given the opportunity to speak before my betters, my sole excuse is that my text is simple and my speech shall be brief. A layman in research! What is a layman doing in any such job? Well, for one thing, we started it, and I suppose now I must come and ask uncomfortable questions in order that some consideration be shown to us—that our part may not be forgotten.

The honor which your organization offers to the Tanners' Council in asking me as chairman of the Research Laboratory Committee of that body, to tell you something of what we are undertaking is most heartily appreciated.

At the outset, may I affirm my very thorough understanding that your Association, in thus asking for our story of the Research Laboratory, looks through and beyond all personality, and that in

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the opportunity you offer me you pay tribute to the clear vision and splendid backing of the men of the organization which I happen to represent, in their foundation of a work, which, we all trust, is to continue to grow in the spirit in which it was founded. Guided by the light of pure science, nurtured by unselfish men, their sole desire is that the truths which may there be developed shall be for the benefit of a common brotherhood, which knows no national boundaries.

The story of the Research Laboratory is known to some of you. How after small beginnings hampered by the exigencies of war and, the Winter of 1920-1921 found the Committee in charge coalescing with the University of Cincinnati. And, Gentlemen may I say in passing, that since our association with Cincinnati, every month has convinced us that we made no mistake in choosing that center of learning. Without red tape, welcomed with broad-minded liberality, solely with the provision that in its study of the underlying principles of the raw materials of our business, and the vital processes of manufacture, the results of our research be treated as all broad-minded scientific research should be—for the benefit of all—the Research Laboratory of the Tanners' Council of the United States, found a permanent home in the Medical School of the University, although under the direct supervision of the dean of the Engineering School.

There, its work has been watched over with steadily increasing interest. These men, deans and doctors, pure scientists, men steeped in the study of abstruse and difficult problems, have watched a great industry, to which civilization pays tribute, a necessary industry in its ultimate definition. We come to the doors of their college and say "give us of your knowledge and we will fulfill your condition," and it is our firm belief that in that instant the vitality and enterprise of our great trade expressed itself. A great step had been taken—the forward movement had begun. I am old enough to realize how great a step that is. I recall that during my younger days in the leather business, if two men sat down to discuss processes, it was a pretty sure bet that within a half hour there would be two angry men. There was no such thing as co-operation and it is within less than the present generation that we have seen the beginnings of real co-

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operation, and now the fruition, which I am very happy to say you men have so ably supported.

One of our American engineers, himself the head of a renowned institution that has a great record of service, holds that every calling becomes of greater service and rises in popular estimation as it lifts itself from the mire of empiricism and rests its work on the solid ground of science.

Medicine and engineering and similar professions have increased their usefulness and prestige in proportion as the chemist, the physicist, the anatomist and other workers in pure science have furnished scientific facts, and as these professions have been able to apply them. So we, in the leather and allied industries, have come to the point where we say to the scientist, "apply your methods and we will heed them; give us facts and we will square our practice with theory which you must prove sound."

And here enters the layman with his contribution, for his function is to act as ballast to the scientist, to keep his feet on the ground, and to provide the co-ordination which justifies the results of combined forces of theory and practice.

A great English historian and novelist pays high tribute to you scientific men, for he says that when the intellectual history of the time comes to be written, nothing will stand out more strikingly than the empty gulf in quality between the richly fruitful scientific investigations that are going on, and the general thought of other sections of the community. In their field they think and work with intensity, integrity, breadth, boldness, and thoroughness, which puts their work out of all comparison with any other human activity. Well, be it so, still must the lay mind hold its own, for with all due respect to Mr. Wells, we must foot the bills.

And may I emphasize the great truth which lies at the bottom of all this endeavor, that whatever our research develops, to be of service to our time and to give a reason for our being, must square itself with sound economic laws, it must be worthy of effort. And if I were to wish for any particular message to leave with you men to-day, it would be that one sentence, that what you are doing, to be of value, must square itself with sound economic laws.

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We are trying to find the laws which will conserve our raw material for the purpose for which we intend it, that thereby a world's population may be better served through our combined efforts; that so far as we can effect it, waste in our industry shall be reduced to a practical minimum—mark that word practical, for that is the layman's text; that all we do shall stand the test of service, our belief is that the leaven which shall effect the perfect blend of layman and scientist is this test of service. Will it work?

It has been my experience of 35 years in my trade that for hard-headed conservatism, we head the list, and therefore it is with a sort of joyful enthusiasm that I view such men confidently backing what we are pleased to call pure scientific research.

What a vision! And with what appreciation should you men view such wholesale conversion. And do not misunderstand me; it is not the enthusiasm of the moment; it is not the excitement of doing something novel, but born of earnest conviction. We feel that your position is now one of great responsibility, and we lay on your shoulders the burden of our questions. What have you to say?

There are serious questions pressing for answers in all branches of our trade to-day. On your side, you have the technical problems. On our side, we have the economic problems. We don't propose to have you men get so far into your laboratories that you can't march out into the tannery and answer our questions. "Will it work?" That is the question!

Suppose you do solve the questions which we put up to you, what is your reward? Well, your reward must be what we can afford to pay—and what can we afford to pay? Are we warranted in calling in men who spend six or seven years in training to merely reach a point where their minds can grasp our problems?

You know adversity is a hard master. We don't do the things we like to do unless conditions are right, and when these problems are put up to us, if we can well avoid them, all right; but to-day there is no avoidance. We are face to face with the situation.

Gentlemen, we can afford to pay what you will let us pay. Do you not see that we must see eye to eye; that laymen and

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scientist must march together; that our future is indissolubly bound together, but that the essence of the bond is mutual confidence in a future that will bring a commensurate reward?

So far, during a period of years, the tanning industry has not earned more than day's wages on the capital invested. Some men think that a reason may be found in the fact that our industry has never been a contributor either to the scientific or economic field of our endeavors. If that is so, is it not time to change? I repeat, sound science presumes sound economics. May we not be at fault somewhere?

I recall one day sitting in the laboratory at Cincinnati and trying hard to understand just what Mr. McLaughlin was trying to explain in what to him was doubtless very simple terms, when one of the professors in chemistry came in and after some general conversation remarked innocently enough that the leather industry had never been a contributor to its particular branch of scientific development, but always a follower, and he hoped for great things from our research work.

Well, I didn't say how much I hoped from that research work, but from my soul I realized that we must get great things. The years of empirical work, the history of tanning from the Pharaohs down, seemed suddenly rolled into that casual talk, and at last the American tanner had realized that he could call science to his aid, and possibly some of these days in the future we may define our business as a science, rather than an art.

You know that "needs must when the devil drives." What have we contributed from the economic side? In a highly speculative business, our records show, as I have quoted, hardly a day's wages earned on the capital invested, and in that time we have exploited (for one branch of our business at least) the forest resources of a nation in ruthless fashion. We have had abundant and cheap raw materials so that we could without effort command the world market.

To-day that condition is changed. We are importers of both hides and tanning materials; our natural resources are dwindling and now at last we talk conservation. Let us wake up to this fact that the old order changeth for others are not sleeping.

The research laboratory is only a beginning, but a good one. We will not be able to judge how well we have built for some

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time yet, but this I can say—that we who have set our minds to this work are going on, and that as fast as facts are demonstrated we are planning to set them forth plainly and simply.

I do not think it too much to say that the care and thoroughness of our technical problems have served as an inspiration in our effort to solve our economic problems in the leather trade; one view must react on the other, and I look to see the results of our co-operation in one direction reap decided results in the other, and I am persuaded to leave with you a modern conception of industrial success—a true union of layman and scientist—An editor of one of the technical papers has expressed the idea very well,

The old way was the lazy way. Put your competitors in a hole: succeed by some trick. Tradition ruled. Have everything locked up tight in front, while a slow but constant leakage went out of the back door. Pay $50,000 a year for legal advice and $5,000 for scientific guidance.

The modern way is to aid the industry in which you are engaged by every possible means; to scorn secrecy as bad form and the weapon of the incompetent, and then, have wits enough to keep ahead of the game.

I appeal for your vision and your enthusiasm for we need it sorely. Never has a more willing ear been turned toward you; never have your opportunities been greater. Whatever the past may have held, we turn toward a brighter tomorrow with a broader vision of co-operation and mutual service.

ABSTRACTS

Proteins and the Theory of Colloidal Behavior. A review by JEROME ALEXANDER in *Chemical and Metallurgical Engineering* 27, 368 Aug. 23, 1922, of the book of the above title by Dr. Jacques Loeb is given as follows:

Besides presenting in convenient and coherent form his ingenious and extensive researches on proteins (chiefly gelatine, albumin and casein) which have appeared in journal articles over a long period, the author in this book gives many hitherto unpublished experiments to support his views.

The first part of the book "furnishes proof of the stoichiometrical character of the reactions of proteins;" the second part gives a "theory of colloidal behavior based on Donnan's theory of membrane equilibria." "Any rival theory which is intended to replace the Donnan theory must be able to accomplish at least as much as the Donnan theory—*i. e.*, it must

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give a quantitative mathematical and rationalistic explanation of the curves expressing the influence of hydrogen-ion concentration, valency of ions and concentration of electrolytes on colloidal behavior and it must explain these curves not for one property alone but for all the properties, electrical charges, osmotic pressure, swelling, viscosity and stability of solution, since all these properties are affected by electrolytes in a similar way."

But "such an application of Donnan's theory would have been impossible without the stoichiometrical proof that proteins form true ionizable salts with acids and alkalis. What was at first believed to be a new type of chemistry—namely, colloid chemistry—with laws different from those of general chemistry, now seems to have been only an unrecognized equilibrium condition of classical chemistry; at least as far as the proteins are concerned. This does not detract from the importance of colloidal behavior for physiological and technical problems, but it completely changes the theoretical treatment of the subject." Evidently then, as the title indicates, Loeb accepts colloids and offers a theory of their behavior. His book should be read by all interested in the subject.

Because of the high reputation of the author, many scientists will be prone to accept his conclusions without submitting his experiments and arguments to critical examination. Your reviewer feels constrained therefore to point out what appeared to him to be some basic errors, both experimental and rational, which strike at the very root of Loeb's conclusions.

Loeb's whole thesis is based on the formation of true ionizable protein salts—*e. g.*, gelatine chloride and sodium gelatinate. This naturally assumes that gelatine is a definite chemical entity, which no one has ever demonstrated. In fact the existing evidence is to the contrary. Thus, the analyses of Levene, Skraup and von Biehler, Dakin, Bogue and others differ widely. But Loeb has failed to define exactly the *quality* of the gelatin he has used. He describes it (p. 35) as "commercial powdered Cooper's gelatine, which happened to have a p^H of 6.0 to 7.0," but before using it he brought it to the isoelectric point and purified it by treatment with M/128 acetic acid. Nothing is stated of the percentage of gelatoses or of gelatones in the purified product, nor is the jelly-strength or mutarotation (after C. R. Smith) given, from which a rough idea of their percentage might be formed. The gelatine apparently lost 20 to 25 per cent during purification, which introduced a like error into some of Loeb's earlier experiments. (See *e. g.*, Harvey Society address, *Science*, N. S., Vol. 52, p. 451 (1920); *J. General Physiol.* Vol. 3, p. 89 (1920); also the present book, (p. 58).

Again Loeb has failed in each case to define exactly the ash and moisture content of the gelatine used, both being essential (especially the latter) in fixing the percentage of gelatine in solution. C. R. Smith, *J. Am. Chem. Soc.*, Vol. 43, p. 135 (1921) and Miss A. M. Field, *ibid.*, Vol. 43, p. 607 (1921), had shown how to prepare ash free gelatin, which is by no means identical with isoelectric gelatin. Loeb gives (p. 35) "a result of an ash determination made by Dr. D. I. Hitchcock on a sample of gelatine

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selected at random" from one of Loeb's stock solutions containing 12.69 per cent gelatine. The analysis showed about 0.1 per cent ash, apparently $Ca_3(PO_4)_2$. Loeb says this amount of ash is without influence, but since C. R. Smith has shown that Ca may exert a powerful influence, it would have been better had Loeb determined the ash of *every* specimen of gelatine he actually used. The paper of Oakes and Davis (*J. Ind. Eng. Chem.*, Vol. 14, p. 706, 1922) also shows the importance of "ash."

Loeb's experimental results are reported mainly in curves or graphs which your reviewer believes are incorrectly plotted and drawn. This is quite evident in the graphs of Chapter VI, where *equal* increments on the axis of abscissas are given M/2, M/4, M/8, M/16, M/32, etc. It is not so obvious in the other chapters where equal increments are given p^H values of 1, 2, 3, 4, 5, 6, 7, etc., because most readers do not stop to consider the real meaning of p^H. This abbreviation of Sorensen is an inverse logarithmic value deprived of its minus sign. The following table will give an insight.

p^H value		Number of times the H (or OH) ion concentration exceeds that of pure water
1	.....	1,000,000
2	.....	100,000
3	.....	10,000
4	.....	1,000
5	.....	100
6	.....	10
7	i. e., conc. H and OH = 10^{-7} mols per liter	0 (pure water)
8	.....	10
9	.....	100
10	.....	1,000

Thus, decrease in p^H value means increase in acidity, not in an arithmetical but in a logarithmic ratio. Curves plotted on an arithmetical basis, as are Loeb's are thus logarithmically compressed and deviations there appearing as experimental errors may really obscure cusps or inflections. Loeb's method of plotting is furthermore apt to make the reader forget that values of about p^H 6 to p^H 7 represent an extremely slight acidity N/10 HCl has a p^H = 1.07 and ordinary distilled water in the laboratory (containing CO_2) has a p^H = about 5.5.

Therefore values of about p^H 2 to p^H 3 represent a very high acidity. Curves which Loeb shows with equal branches, resembling parabolas, should rise sharply, almost asymototic to the p^H 4.7 ordinate, and after turning, gradually approach to axis of abscissas. Some other points may be epitomized as follows:

The view (Chapter II) that proteins fix acids by their free NH_2 groups and alkalies by their free COOH groups, while simple, does not accord with the observation that deaminized gelatine (Blasel and Matula) and highly hydrolyzed gelatin (T. B. Robertson) both fix about as

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much acid as the original gelatine. Jordan Lloyd and Mayes (*Proc. Roy. Soc.*, B. Vol. 93, p. 69, 1922) give additional evidence that disproves this appealing but incorrect chemical explanation.

Loeb's interesting qualitative experiments (Chap. II) show, as Bancroft remarked, that acid or plus-charged gelatine (p^H less than 4.7) fixes only anions, while alkaline or minus-charged gelatine (p^H more than 4.7) will fix only cations, which is only to be expected. Clay or fine silica might act similarly.

His quantitative experiments (Chap. IV) show *e. g.*, that the number of cc. of different N/10 acids required to bring isoelectric gelatine to the same p^H varies roughly in accordance with the p^H (available or effective acidity) of each acid at that p^H. Thus at p^H 3 the effective acidity of HCl and H_2SO_4, oxalic, and phosphoric acids are about 3, 2 and 1 respectively and Loeb found that to bring one gram of isoelectric gelatine to p^H 3, it took (in cc. of N/10 acids) 7.2 HCl, 7.5 H_2SO_4, 13.15 oxalic, 20.7 phosphoric. Most of his experiments stop at about p^H 2, which represents an acidity equal only to N/100 HCl (p^H 2.02).

Assuming that deviation from the curves is due only to experimental errors, these results, while not inconsistent with the view that chemical compounds have been formed, may simply be due to the fact that within the p^H range of the experiments, gelatine has, at each p^H, a more or less definite free adsorptive surface and adsorbs acids in proportion to their free field of force. The fact that material chemical changes (see above) in gelatine do not affect its acid combining capacity appreciably favors the adsorption rather than the chemical view. Even W. B. Hardy (see Loeb, p. 9), who latterly expressed belief in salt formation, stated that the reactions are not precise. No one has ever prepared chemically pure gelatine, and estimates of its combining weight vary from about 768 (Procter and Wilson) to about 96,000 (C. A. Smith). Jordan Lloyd gives chemical evidence that it cannot be less than about 10,300 and Loeb apparently believes it to be between 12,000 and 25,000. As Hardy indicates, it depends upon conditions, and your reviewer believes it will also vary with the kind of gelatine. It is still to be demonstrated that these compounds possess the definiteness which is at present connoted by the expression "chemical compound."

The p^H (that is, the effective reaction) of acids is controlled by the specific nature of their anions; the p^H of alkalis by the specific nature of their cations. The p^H of N/100 HCl is 2.02, but the p^H of N/100 acetic is 3.37. Why? Because in aqueous solution Cl releases H+ more readily than does CH_3COO—. This means that HCl is a strong acid and acetic a weaker one.

Hofmeister, Ostwald and M. H. Fischer observed the effect on proteins, of *equal molar concentrations* of various acids and alkalis and then compared the consequences of their *differing* p^H *or effective reaction.* Loeb, on the other hand, uses enough of various acids and alkalis to make their *effective reactions* (p^H) *equal* and then compares the *varying quan-*

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tities required. What he considers "practical identity"—*e. g.*, in curves of Figs. 19 and 20 (pp. 79 and 80)—may appear differently if the curves are correctly plotted. He even comments (p. 80) on the anomalous behavior of acetic acid, probably caused by sol formation (see below).

That the problem of the swelling of gelatine in acids is not as simple as a Donnan equilibrium formula would indicate is evident from the work of A. Kuhn (*Kolloidchem. Beihefte*, Vol. 14, p. 202, 1921), who found it to be dependent upon four factors:

A (*1*) Hydration (simple swelling)
B (*2*) Sol formation (incidental peptization)
(*3*) Hydrolysis
C (*4*) Dehydration (flocculation)

The maximum is reached when, with increasing concentration of acid, hydration is overbalanced by sol formation and hydrolysis. Probably it was sol formation that caused Loeb to lose about 20 per cent of his gelatine in his earlier experiments (p. 58). Since sols (as Graham distinctly pointed out) do diffuse, albeit though slowly, we have here another factor working contrary to the Donnan equilibrium. Experimenting with fifty organic acids, Kuhn could not decide if the combination was chemical or adsorption.

Loeb argues (p. 16) that "if the addition of a salt to a protein solution diminishes its osmotic pressure by causing an increased formation of aggregates, the same addition of salt should increase the viscosity of such a solution. The reverse, however, happens, the viscosity of the solution being decreased by the addition of salt." Loeb here entirely overlooks the existence of the zone of maximum degree of colloidality. (See *J. Am. Chem. Soc.*, Vol. 43, p. 434, 1920). Viscosity does often increase as particles aggregate, as in cooling gelatine solutions, but viscosity may also increase as particles are dispersed, as when cream is homogenized, or karaya gum dispersed.

Loeb makes the sweeping assertion (p. 278) that "there is only one source of colloidal behavior—namely, the Donnan equilibrium—at least as far as the proteins are concerned." Donnan can hardly believe this, for Loeb quotes him (p. 22) as saying (*J. Chem. Soc.*, Vol. 105, p. 1,963, 1914) that in the comparatively simple case of a copper ferrocyanide membrane and potassium ferrocyanide solutions, "the phenomena are not so simple as supposed in the theory." The great danger of applying mathematics to chemical and physical problems lies in the fact that we may be blinded by the logical perfection of this mere tool and make erroneous assumptions, or else neglect important factors which so often crop up unexpectedly in nature. The fact that some of the assumptions involved in Donnan's equations do not apply to gelatin has been pointed out by Jordan Lloyd—*e. g.*, the gelatine "ion" does diffuse. The basic assumption that a true hydrolyzable "salt" is formed is, to say the least, doubtful.

A word in defense of Thomas Graham is necessary, for his classic papers are seldom consulted in the original. Loeb states (p. 275): "Graham

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had suggested the distinction between colloidal and crystalloidal substances, but it was found later that one and the same substance—*e. g.*, NaCl, may behave when in solution either as a crystalloid or a colloid. It was then proposed to drop the distinction between colloidal and crystalloidal substances, and distinguish between the colloidal and crystalloidal state of matter." This is surprising, for Loeb on page 1 quotes from Graham the very paragraph wherein the word "colloid" was born; the particular sentences of Graham are: "As gelatine appears to be its type, it is proposed to designate substance of the class as colloids and to speak of their peculiar form of aggregation as the colloidal condition of matter. Opposed to the colloidal is the crystalloidal condition. Substances affecting the latter form will be classed as crystalloids. The distinction is no doubt one of intimate molecular constitution." Furthur on in the same paper, "Liquid Diffusion Applied to Analysis" (1861), Graham says: "The mineral forms of silicic acid, such as flint deposited from water, are often found to have passed during the geological ages of their existence from the vitreous or colloidal into the crystalline condition (H. Rose). The colloidal is in fact a dynamical state of matter, the crystalloidal being the statical condition." And still further: "The inquiry suggests itself whether the colloid molecule may not be constituted by the grouping together of a number of smaller crystalloidal molecules and whether the basis of colloidality may not really be due to this composite character of the molecule." So Graham did know that the same substance can exist in both colloidal and in crystalloidal state. Modern research has fixed dispersion into particles between about 100 $m\mu$ and 5 $m\mu$ as the criterion of the colloidal condition, and the particles may be crystalline or consist of random clusters. But these statements of Graham still hold true.

It is to be regretted that Loeb did not review, discuss and consider the results of many important workers in this field. Thus he does not mention Blasel and Matula, Arisz or Jordan Lloyd and dismisses C. R. Smith with mere mention in a footnote (p. 36) and Wo. Ostwald and Martin H. Fischer in a brief quotation from Zsigmondy (p. 76). He quotes and demolishes Pauli, with whom Ostwald and Fischer likewise disagree. All told, Loeb's book is written from the standpoint of an advocate pleading his cause, rather than from that of a judge deliberately weighing all the evidence, and this brings inherent weakness.

Degreasing of Skins. By E. Andreis. *Le Cuir*, **11**, 158-63 (1922). The modern demands for leathers of fancy finish require a thorough degreasing of greasy skins such as those of the sheep and pig especially. The old methods using acids and alkalis with pressure cause losses in hide substance and are injurious to the structure of the skin. Agents such as chalk, plaster, silica and clay are very inefficient and also damage the skin. The practice of degreasing the tanned skin is indeed a poor one as the grease seriously interferes with the tanning often making retannage necessary. The fallacy of considering the degreasing after the skin is tanned as a simplification is due to a false idea of the nature of the grease in sheepskins. The grease of the skin and especially that of the wool

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is a complex mixture of free fatty acids, esters of the same nature as those of wax and of unsaponifiable material. It contains myricyl, carnaubic, lauroceraric, lanopalmitic and small quantities of volatile acids; it is rich in higher alcohols such as cholesterine and isocholesterine.

The only logical procedure is to degrease the skins before tanning. Degreasing by pressure is not complete but will suffice if the skins are not extremely greasy. Complete degreasing may be effected by extraction but this requires expensive installation. In Argentina the two processes are combined. The skins after dewooling by sweating are extracted in a zinc lined metal drum with benzene and methyl alcohol, the latter being added to carry the benzene into the damp skins. After 1 to 1½ hours the skins are removed, quickly pressed, limed and worked as usual giving excellent leather without grease stains.

The usual installations for extraction are costly. An inexpensive automatic extraction apparatus is described. The skins are placed in a wooden drum with strong spirits of wine and benzene. The alcohol extracts the grease from the wet skins and in turn gives it up to the benzene separating into two layers. The drum is hermetically sealed and supplied with the solvent from an overhead tank. The grease-benzene solution is siphoned off the drum passing down into a steam chamber where the grease collects and the solvent vaporizes. The vapors pass up to an overhead condenser and back into the solvent tank thus completing the circuit. The loss of solvent is practically negligible and there is no danger of explosions. R. W. F.

The Use of Orpiment. By P. Huc. *Halle aux Cuirs*, June 18, 1922, 175-77. During the war the scarcity of orpiment made it necessary to substitute sodium sulphide. While the action of this agent was no doubt rapid enough it often caused undue swelling and consequently serious damage to the quality of the leather. In advocating a return to the use of arsenical limes for fine skins, provided a reasonably uniform arsenic sulphide is available, the author describes strictly comparable experiments on unhairing with lime and with arsenical limes which emphasize the well known advantages of the latter. In all cases the time of liming is materially shortened with the arsenical limes giving also normal plumping, excellent suppleness and fine grain. Various arsenic sulphides were tried but the yellow orpiment gave the best results. It is suggested that the limes be made up as follows: Weigh the quicklime, add to it from 0.8 per cent to 1.2 per cent of its weight of yellow orpiment according to results desired and then add water slowly until just slacked. Finally make up the lime with water as usual. R. W. F.

Report of the Committee on Leather Analysis. By M. Chambard. *Les Industries du Cuir*, p. 229-35 (August 20, 1922). Samples of three leathers of the same tannage were analyzed by five laboratories. The agreement between the results for hide substance and water solubles was satisfactory, although the details of each method might well be studied. The results on ash and grease (petroleum ether extract) were very unsatis-

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factory, and these methods need careful study. The sample of leather must not be too small and the association should specify how samples are to be taken. I. D. C.

Montan Wax and Polishing Creams. By P. Huc. *Industries du Cuir,* 217-21 (July 16, 1922). Lignite or montan wax is a dark odorless brittle wax melting at 80°-90° extracted from lignite by volatile solvents. The author has found benzene boiling under pressure the best solvent.

It contains 30 per cent unsaponifiable material which is emulsified by the saponified portion. A yellowish white wax is obtained by refining, but this darkens considerably and develops an oder on aging. The wax is formed of equal parts of a fatty acid (montanic acid $C_{28}H_{56}O_2$) and an alcohol of which little is known. Lignite wax increases considerably the melting point of soft waxes but its use is limited by the fact that the commercial material contains impurities or adulterants (carbon, chalk, barytes, resins, bitumen, etc.).

The creams are pasty solutions of wax in a volatile solvent colored and scented with nitrobenzene. After applying to leather and polishing the wax should not take the imprint of the fingers and should not crack. This can only be obtained by using brittle waxes with a high melting point such as carnuba or lignite. The cream can best be manufactured in an auto-clave provided with a stirrer as by this means loss of solvent and danger of fire is avoided.

In preparing small amounts of the cream the author used an electric iron set in a sheet iron box, the latter having holes in the bottom to allow the melted wax to drop into the solvent. The iron and box were enclosed in a large covered porcelain dish. The following formulae for black crèmes were found to be satisfactory.

(No. 1)	Lignite wax	100 grams
	Paraffine	85 grams
	Stearate of nigrosine	25 grams
	Turpentine	425 grams
(No. 2)	Lignite wax	10 grams
	Carnuba wax	4 grams
	Paraffine	14 grams
	Nigrosine	3 grams
	Turpentine	66 grams

Since lignite wax darkens in the air it causes an undesirable darkening of colored creams. But an effort should be made to use this wax in place of the imported carnuba or candelilla waxes.

I. D. C.

A Modern Tannery. By George Chevraux. *Le Cuir,* 11, 240 (1922). In building a modern tannery the latest improvements in machinery, etc., should be carefully studied and installed. Machinery should be placed so that supervision of the workers is easy. The workrooms should be light, airy and not crowded. In selecting a location consideration should be

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given to shipping facilities, water supply, drainage and room for expansion. The financial end should be carefully studied and an excess of capital of about 40 per cent should be provided for emergencies.

I. D. C.

The Determination of Formaldehyde in Impure Solutions. By Fr. Kuhl. *Coll.*, **625**, 133-42 (1922). The following four methods were compared by using each to analyze a formaldehyde solution in a concentration of 40 per cent, 1 per cent and 0.1 per cent. (1) Sulfite method (Auerbach: *Arbeiten a. d. Kaiserlichen Gesundheitsamt 22*, 584). If formaldehyde is treated with sodium sulfite, the following reaction takes place:

$$Na_2SO_3 + CH_2O + H_2O = CH_2OHNaSO_3 + NaOH.$$

Then the sodium hydroxide can be titrated with standard acid. This method was fairly satisfactory for the 40 per cent and 1 per cent solutions but not for the 0.1 per cent solution due to a bad end point. (2) Hydrogen peroxide method. This depends on the fact that formaldehyde is oxidized to formic acid in alkaline solution in the presence of hydrogen peroxide. Blank and Finkenbeiner's method (*Ber.*, **31**, 2979) gave low results since the oxidation is very slow in the cold, but Ullmann's modification (*Org. Chem. Praktikum*, p. 152) in which the solution is heated for 25 minutes at 100 degrees gave good results. (3) Romijn's iodine method (*Zeit. f. analyt. chem.* **36**, 18). By this method formaldehyde is oxidized to formic acid in alkaline solution and the excess iodine titrated with thiosulfate. (4) Romijn's potassium cyanide method. (*loc. cit.*) $CH_2O + KCN = N:C.C:H_2OK$. The determination is carried out as follows: 10 cc. of cyanide solution (6.2 grams KCN per liter) and a definite volume of the formaldehyde solution are measured into a 50 cc. volumetric flask. After standing a few minutes 10 cc. of N/10 silver nitrate and three drops of 50 per cent nitric acid are added, and the flask filled to the mark with water. The solution is then filtered and 25 cc. of the filtrate titrated with N/10 potassium sulfocyanate. A blank must be run in same way and subtracted. One cc. of N/10 silver nitrate = 3 mg. formaldehyde. Methods 3 and 4 were both satisfactory for pure formaldehyde solutions.

Used formalin solutions contain amino- and oxy-acids which react with peroxide to form carbon dioxide, acids or aldehydes, (*Coll.*, 1921, p. 161) therefore Method 2 can not be used for impure solutions.

Iodine was found to react with the amino-acid, alanine and with oxy-acids. Therefore only the potassium cyanide method (4) can be used for impure formaldehyde solutions. Only the free formaldehyde is determined by the cyanide method; not that loosely bound to amino-acids according to the reaction: $CH_2O + RNH_2COOH = RNCH_2COOH + H_2O$.

I. D. C.

Contributions to Tannin Analysis With Special Consideration of Gambier Extract. By L. Pollak. *Coll.*, **625**, 125-33 (1922). To obtain a non-tannin solution from gambier extract that will not react with gelatin solution or iron is difficult by the filter and impossible by the shake method. Kubelka and Köhler (This Jour., **16**, 388) recommend a double detannization in such cases. Since their experiments were incomplete

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Pollak carried out a series of experiments with samples of "asahan" gambier extract produced during 1919, 1920 and 1921.

Series A. Four extracts were analyzed by: (I), the official shake method, (II), the official method with double detannization, (III), the shake method, shaking for one-half hour, (IV), the shake method using 8.5 grams of hide powder, (V), the filter bell method. Neither a longer period of shaking or more hide powder influenced the results. The results by (II) were higher than by (I), and between those by (I) and (V).

Series B. Five extracts were analyzed by: (I), the official method, (II), the official method with double detannization, (III), the official method with triple detannization, (IV), the filter method. The results by (II) are again between those by (I) and (IV). The results by triple detannization are not higher but agree within the limits of error with the results by double detannization. An end point in the adsorption is therefore reached by double detannization.

Series C and D. Procter has stated that heating increases the quantity of tannin in gambier solutions. To investigate this point gambier extracts were analyzed by the filter method, (a) after heating in the water bath one hour (b) after heating in a pressure flask at 120 degrees for one-half hour and (c) without heating. There was no increase in percentage tannin due to heating. It is possible that the shake method is responsible for the belief that long heating increases the tannin in gambier solutions.

That the filter method gives values which agree well with those found in actual tanning is shown by the following experiment: Twenty-five pieces of sheep skin (38 kg.) were tanned with gambier extract and a little pine bark liquor. The amount of gambier tannin found in the leather was, by the filter method, 25.48 per cent and by the shake method 24.15 per cent. The amount of gambier tannin used, calculated from the analysis of the fresh and used liquor was by the filter method 26.98 per cent and by the shake method 20.65 per cent. By the filter method therefore, 94.44 per cent of the tannin used was found in the leather, while by the shake method 116.95 per cent was found. By the shake method with double detannization 103 per cent of the tannin used was found by analysis of the leather.

I. D. C.

The Chemistry of Salt Stains and Salt Damages. By W. MOELLER *Zeitschr. für Led. und Gerb. Chem.*, 1 210 (1922). The causes of salt stains can be exceedingly numerous and it is doubtful if a single agent exists which will prevent all these damages. Among the various forms of salt stains those which are produced from tyrosine by a ferment, such as the so-called tyrosinase, are especially irksome. Collagen is free from tyrosine and hence is not a factor in producing such stains but the muscle fibers, nerve and blood vessels and especially the constituents of blood and lymph produce tyrosine as a cleavage product. Gessard [*Compt. rend.*, **130**, 1327 (1900)] has observed that a primary red oxydation product was produced by the action of tyrosinase on tyrosine and this red product was changed immediately into melanine by the salts of the alkaline earths and heavy metals. Haehn (*Koll.-Zeitschr.*, **29**, 125) states that

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pigment colors can be formed with free tyrosine with the help of tyrosinase, which range from red through brown and violet into pure black.

The author assumes that the basic cause of all salt stains is fermentative splitting and hydrolytic decomposition. Since the method of Paessler, using soda ash with salt in salting, finds favor and gives good results in practice, the hydrolysis of hide powder by these materials was investigated. The action of a mixture of sodium carbonate and sodium chloride on fibrin was also investigated. It was found that sodium carbonate and the acid carbonate caused practically no hydrolysis of hide powder which is surprising for sodium carbonate as a contrast to the action of other alkalies. The mixture of sodium carbonate with sodium chloride and with sodium sulfate gave results which indicate that sodium carbonate repressed the hydrolytic action common to these salts. Therefore the author claims that there is a sound scientific reason for the use of sodium carbonate in admixture with common salt in the salting of hides in order to prevent salt stains and damages. G. W. S.

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The American Leather Chemists Association

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WILHELM FAHRION

Dr. Wilhelm Fahrion died on February 21st at Feuerbach near Stuttgart at the age of 58. Dr. Fahrion was, without doubt, one of the greatest oil chemists of his day, moreover, he was very prominent in the field of leather chemistry. His publications on the theory of leather formation are well known. Besides the theoretical questions, the practical side of our industry also engaged his attention and various patents were obtained by him on aldehyde and chamois tanning. His interest in the analytical side of our science is evidenced by his test for the water resistance of leather. Fahrion was the editor of *Chemischen Umschau* a technical journal for the fat, oil and resin industry.

His contributions stand as testimony of his services to science and industry. He is held sacred in the memory of his colleagues.

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ADOPTION OF METHODS

The proposed methods for Moisture, Ash and Unsaponifiable in Sulfonated (Sulfated) Oils [See This JOUR., **16**, 525 (1921)] were adopted as official by a vote of 27 to 1. The proposed alterations and additions to the provisional methods for the Analysis of Sulfonated (Sulfated) Oils [See This JOUR., **16**, 526 and 657 (1921)] for the Analysis of Sulfonated (Sulfated) Oils were adopted by a vote of 28 to 1.

"PURITY" OF TANNING MATERIALS

In reply to the request for statements of opinion on the proper manner of calculating "purity" of tanning materials the following expressions have been received:—

"Purity" is the percentage of tannin in a material, based on the "solids" contents. Whether this basis should be the total or soluble solids depends entirely upon what the user of the material in question desires to know.

By using the total solids as a basis the amount of insolubles is entirely disregarded, as illustrated in the following examples of two widely different extracts of quebracho, one being a typical analysis of an ordinary solid and the other a clarified one and in which the "purity" figures are exactly the same. The only value this figure has is to give the percentage of tannin in the total solid matter.

	Ordinary %	Clarified %
Total solids	80	80
Soluble solids	72	79.5
Insolubles	8	.5
Non-tannins	7	14.5
Tannin	65	65
Purity	81.2	81.2

On the other hand, by using the soluble solids as a basis on these same extracts, we find that the "purity" of the ordinary extract is 90.3 and of the clarified, 81.8. This method of calculation is a direct indication of the proportion of non-tannins and is perhaps of greater value to the user, particularly in yard liquors.

In either case, the "purity" figure is not an essential but merely a convenience, as the regular analysis shows these conditions in a little less tangible form. If this reading is desirable, which is

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doubtful in the writer's mind, it would seem that the burden of evidence is in favor of the "soluble solids" basis, as the proportion of non-tannins present, particularly if the character of the tanning material is well-known, is of considerable interest.

Roy H. Wisdom.

The term "purity" was coined years ago to represent a method of expressing the ratio existing between the tanning matter and non-tanning matter in a tanning liquor. The ratio was used for the purpose of giving some sort of classification other than specific gravity to the various liquors used in the tan yards of that day, and was later extended to tanning materials and tanning extracts. Although the term was used to indicate relative tannins and non-tannins, and hence soluble matters, "purity" was originally figured by dividing the tannin figure by the soluble solids figure. Mr. G. A. Kerr, in a committee report published in the JOURNAL of the A. L. C. A. in 1906 (page 91), speaks of "the purity, or ratio of tannin to soluble solids."

The term "purity" conveys to the average layman an indication of the rapidity of the tanning action of a material, and of its relative non-tannin content. Thus, quebracho is known as a high "purity" material, while oak and hemlock are known as relatively low "purity" materials. The ratio is useful, and except in a few cases, will give fairly relative figures.

Originally, the purity was figured by dividing tannin by soluble solids, but latterly, some chemists have used the total solids figure as the basis, so that at the present time some confusion exists as to the proper method. If the term is to be used in connection with our work, there of course should be uniformity in computation.

The original method of figuring by using soluble solids as the base, seems to me to be the proper method; while the insolubles undoubtedly have a mechanical effect on the rate of tanning, it is not apparent that this mechanical effect should be given the same relative weight that is given the chemical or physical characteristics of the material. Moreover, the soluble solids figure, and the tannin figure, have both been arrived at in our method of analysis, after giving effect to the insolubles

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figure. If the insolubles are high, the soluble solids and the tannin are both affected, and any figures based on their ratio are accordingly changed. So that when total solids basis is used for purity, the effect of insolubles is multiplied or at least increased. Because the insolubles represent matters insoluble in a solution of the concentration, and at the temperature prescribed by the analytical method, and do not always represent the concentration and temperature conditions of practical tannery operation, it may be argued that for that reason soluble solids should be eliminated as the basis for purity computations. The definition of insolubles as shown in an analysis is generally understood, and if "purity" is based on the figures shown by an analysis we cannot with propriety introduce an outside factor not indicated by the analysis, and which varies with different materials. In extracting raw tanning materials, fine particles of the material extracted are generally present in the extractive matter, and when the total solids figure is used as a basis for figuring purity, these particles affect the result and occasionally a ridiculous purity figure is produced. If the insolubles are inert, it should not be possible for them to enter into a relation designed to express the chemical or physical probabilities of a material.

It may be argued that it is necessary to use total solids as the basis in order to register the influence of the insolubles. A sulphited solid quebracho extract containing no insolubles may have a lower purity than an ordinary solid quebracho extract showing considerable insolubles, even when the purity is figured on the basis of the total solids. Admittedly, the "purity" of the ordinary quebracho figured on basis of soluble solids would be even higher, but the illustration will serve to show that purity figured on basis of total solids will not always give effect to the presence of insolubles.

In practical factory control the direct ratio between tannins and non-tannins is sometimes used, and that ratio has advantage over the purity figure in that the ratio is direct between the main factors of a tanning liquor.

When materials of the same character, or liquors of uniform composition are to be compared, a total solids basis would prob-

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ably establish comparable records; but when a purity ratio is to be used on all materials, the original ratio of tannin to soluble solids is undoubtedly preferable.

W. H. Teas.

Speaking as a tanner I desire to state that the amount of insoluble non-tans in an extract is of no great interest to the tanner except as it affects the density of the extract. For tanning purposes they are virtually inert, and to calculate waste matter into the ratio between the useful elements and the tannin is absurd. For drumming purposes the "purity" is of little moment, as "total soluble solids" is more important than purity unless the amount of non-tans is very great. I fancy very little, if any, insoluble matter is worked into the leather in the drum. Even if any is taken up it cannot be driven deeply and would be removed largely in subsequent treatment.

P. M. C. Armstrong.

THE IMPORTANCE OF FINISH IN THE CUTTING AND MARKETING OF SOLE LEATHER *

By *Harrison B. Smith*

When Mr. McLaughlin asked me to speak before the Leather Chemists' Association, I at first hesitated to accept, as I did not feel qualified to talk intelligently on any technical subject. On further consideration, however, it occurred to me that there is a subject which would be of interest to you and one about which I did feel qualified to talk, having had considerable experience in the tannery, and also in the cutting and selling of cut soles and sole leather. The subject is the finish of sole leather. When I say finish, I refer to the appearance of both grain and flesh, the texture and condition of the grain, or in other words, those qualities outside of the weight and selection of the leather which are most important from the viewpoint of a shoe factory buyer.

The average tanner, or chemist in a tannery, is inclined to

*Address to the 19th Annual Meeting of the A. L. C. A., at Bigwin Inn, Ontario, Canada, June 22, 1922.

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devote the largest part of his attention and thought, to plumpness, gains, and the correct flexibility of the leather, satisfying himself with a fairly uniform color, and a reasonably smooth grain. While plumpness and gains are absolutely essential to a successful tanner, I do not think most of them, who have not personally been in touch with the cutting of the leather, appreciate to the fullest extent the bearing the finish has on the ultimate value received for the leather, and the advantage it gives a salesman in competing with a leather of less pleasing appearance.

I do not contend that color in anyway adds to the quality of the leather, but it certainly does add to the value in dollars and cents. There are more light and natural bottoms on shoes to-day, than ever before, and the shoe manufacturer must look for a leather which will give him a uniform run of bottoms on his shoes. Previously, when a large part of his shoes were black bottoms, he could sort out the off colored soles in his racks, and put them into the black bottom shoes, so that he did not have to pay the same attention to uniformity of color when buying soles, as he does to-day, when he will often have orders for nothing but light bottom shoes.

A tanner will make a shipment of leather to a sole cutter, and be well pleased with the appearance of the leather. The leather is cut into soles. Any uniformity of color in the leather is more readily seen when the soles are compared. The individual backs may be uniform in color, but if the different backs vary, it will have the same result when cut into soles as if the back itself was of varied shades. There will be a darker sole on one foot, and a lighter colored one, of perhaps a little different shade, on the other foot. The bottoms on the pair of shoes made with these soles are not alike in appearance. The kick comes back over the way the leather has come, through the sole cutter to the tanner who thinks they are all a bunch of cranks. They may be, but they have to be, for the public demands appearance, and the tanner is the man who can give it. We have been obliged at times to sell cut soles for three to four cents a pair less, on account of mixed color. Taking as an average about twenty pairs of soles out of a back, this will mean 60 to 80 cents a back, or $1.20 to

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$1.60 a hide. A good profit to-day for the tanner, who ultimately suffers. You can drag the hide all over the tannery for a tenth of this amount.

A tanner is usually satisfied with a nice piece of leather in the bend part of the hide, and with fairly good shoulders, necks, bellies, and flanks, which are just as important, and very much more difficult to get right. Two pairs of shoulder soles, stepped down one grade, can mean ten cents on the back, or twenty cents on the hide. Nearly three quarters of a cent a pound on the backs. A poor flank can easily mean from a half to a cent a pound on the backs. Shoulders alone will cut at a difference of three to four cents a pound out of the same hide, and equally weighted leather. On six pound shoulders, this will mean eighteen to twenty-four cents a shoulder, or thirty-six to forty-eight cents a hide. Every pair of innersoles out of the belly, stepped down one grade, will mean two to four cents. A very little apparent difference in the belly, may mean from one to two cents a pound difference in value. Ten to twenty cents on the hide. These figures are worth consideration by any tanner. The cost per pound of tanning is insignificant if the leather cuts poorly. A high cost of the tanning may be profitable if the cutting results are there. While a large part of the finish is obtained by physical treatment of the leather, a lot depends on the chemist and tanner to have the leather in the right condition, so that it will respond to treatment. Cracky flanks, poor grain, wrinkles set in the leather, are all tanning problems.

How many tanners go so far as to find out what their leather does in a shoe factory? How does your leather finish in a shoe factory? Does it wet up right? Does it dry out pliable and maintain its color? Does it leave a deposit of sugar and salts when dried out? Will it buff right, or will it glaze? Is the grain heavy enough to stand fairly deep buffing to get the shoulder wrinkles out? What kind of an edge will it make? All are vital questions in marketing your leather, and giving satisfaction.

We have had soles cut from leather of the best quality, glaze in the factory. A lot of money was spent on the hides for this leather, and a lot more in the tannery. A little thing like not buffing right will throw it out of a factory. We have had soles cut from the best appearing leather we could buy, turn purple

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on the shoes. A great many light colored leathers will turn over to a distinct red when exposed to the light. Others will harden up after being tempered. Some will show the extract on the grain making the leather brittle and dark. The greatest selling point is to be able to say with assurance "I know this leather will finish."

I realize the difficulty of uniformity in a tannery and the constant fight to maintain a certain standard, but the battle is well worth while, and will pay well if you can get the right finish. A very good rule for any tanner to follow to-day, is that most any expense is justified, if it improves in any way the cutting value of the leather. I am not a technical tannery man and cannot help you in arriving at the desired result. I do know, however, the importance of the results, and can only urge all tanners, and chemists, to give more attention to the finish, however much they have given in the past. It will pay and pay well.

I want to thank the officers of the Association for the honor they have given me in asking me to speak at your meeting, and particularly thank the indulgence of those present.

EXTRACTION OF OILS AND GREASES FROM LEATHER*

W. K. ALSOP: Our present method specifies the use of petroleum ether for extracting oils and greases, and it has been recommended to use chloroform in place of it. This Committee undertook to find out which was most suitable for the purpose and in view of the results obtained, the Committee recommends that the Association retain their present method. Several committees have reported on this subject, and have been in favor of the use of chloroform, but the Council of the Association has not been satisfied that it was the proper thing to approve the change.

The Committee found that errors due to the use of chloroform, by reason of its extracting from the leather other substances that were not greases or oils, involves more error than the results obtained with petroleum ether. This report has been published in the "JOURNAL," and I don't believe it is necessary to read it.

* Discussion of the Committee Report at the 19th Annual Meeting. See This JOUR., 17, 292, 1922.

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PRESIDENT SMALL: This Committee Report is worthy of your careful consideration. As Mr. Alsop has stated, a previous Committee recommended that we replace petroleum ether by chloroform as the official solvent for the extraction of oils and greases from leather. The recommendation came before the Council in due course but failed of approval and therefore under the by-laws was not submitted to the Association.

In some quarters this action of the Council was rather severely criticized. In others, the impression apparently was gained that because chloroform was recommended it consequently was adopted by our Association, an error that seems to be rather prevalent among the members of the Society of Leather Trades Chemists. It should be distinctly understood that petroleum ether is the only official solvent authorized in our method for the purpose under discussion.

The report of this year's Committee apparently justifies the action of the Council in withholding approval of the recommendation of the earlier Committee, that chloroform be substituted for petroleum ether. However, the question possibly is still an open one and the Council will be glad to give careful consideration to any arguments you may present at this time.

F. P. VEITCH: I have decided views on this question, but I am not prejudiced in favor of any solvent. I am after the truth only. Now, the facts so far as a study of the subject has developed them are these: Two Committees of this Association and two Committees of the Leather Trades Chemists Association have reported that petroleum ether is not a satisfactory solvent,—doesn't extract all the grease. They have also reported that any other solvent that has been recognized as in some respects preferable has extracted something other than grease. This is the fifth Committee report. Four have been favorable to a new solvent, and only the fifth to the old solvent. If, in the face of four reports, unfavorable to the old solvent, the Council was undecided what to do, it seems to me that they would still be undecided here. I don't think the work done this year conclusive. If I thought so, I would make no comment other than to support the recommendation of the Committee.

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W. K. ALSOP: This Committee does not undertake to say that petroleum ether is the most suitable solvent to extract oil and grease from leather. There may be some more suitable one, but I think that the report is pretty conclusive as to the fact that it is more suitable than chloroform.

A. C. ORTHMANN: I happened to be on the Committee two years ago, and was not in accord with the findings of that Committee. I agree with Mr. Alsop. I still believe that we have about the best solvent that we can get in petroleum ether. I don't believe that we should go to chloroform at all, just because it does extract more than petroleum ether will.

SOME OBSERVATIONS ON THE HISTOLOGY OF BATED SKINS *

By Röhm and Haas Company

The processes of the beamhouse, especially the processes of liming and bating, are as we all know, centuries old, and it is a subject of interesting speculation how they may have been evolved. During the last thirty years they have attracted increasingly the attention of science and while a great deal still has to be cleared up, we understand the underlying principles much better to-day, thanks to the unselfish efforts of men such as Procter, Wood, etc., who have been giving unstintingly to the industry the results of their studies.

One of the most interesting subjects is the bating process, which has puzzled many minds. How many people took a try at it is shown by the many patents purporting to give to the tanner a full-fledged substitute for the filthy, unreliable, dung bates; but most of them have been fundamentally wrong.

A step in the right direction of finding a substitute for the manure bates was undertaken by Salomon in his article in the *Technology Quarterly*, 1892, in which he published the results of his studies on manure bates and bran drenches which he had been studying while working with Professor Eitner in Vienna. He points out in this paper clearly the action of the enzyme in the bating process, but no practical results that would have been interesting for the industry were obtained by him.

* Read before the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Canada, on June 22, 1922, by Charles S. Hollander.

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Subsequently Joseph Turney Wood in his studies on the bating process started out to put to a practical test these "ready-made" enzymes pepsin and pancreatin, but did not find their action sufficient, and abandoned their use for the study of the effect of the bacteria and the enzymes formed by them in animal dung and also the decomposition products of the bacterial action chiefly amino acids.

Dr. Otto Röhm was the first to put on the market a commercial bate consisting of a "ready-made" enzyme such as pancreatin, mixed with a deliming agent, and of absolutely standardized composition. His type of enzyme bate has replaced the dung bates practically everywhere.

While we all know to-day in a general way that the function of the bate is to delime the skin *and* to digest certain parts of the hide substance, we cannot yet say with accuracy what is being digested and how far. In this case, as so often in the history of industry, practice marched ahead of theory and the beamhouse foreman had to go through the painful experience of eliminating one mistake after the other by sheer power of observation. We chemists should never forget that this man without the aid of science has surpassed most of us in the power of observing details which would seem entirely irrelevant in the eyes of us theorists, but by doing so, by using the indicators that nature gave him, in his sense of touch, of smell and taste, he was able to conduct operations on as vast a scale as 2,000 dozen skins a day without a mishap. He used his finger tips to tell him when the grain was smooth enough and when the skin was soft and pliable enough to be considered "down," and also to determine with marvellous accuracy the temperature of his bating liquor. He used his sense of smell to judge very accurately indeed the presence or absence of the right kind of fermentation, and sometimes his sense of taste to maintain the right amount of alkalinity or sweetness. I know a beamster who, whenever a correction had to be made in this latter respect, picked up a bunch of limy hair from the floor and put it into the paddle to restore the sweetness to the right degree. His explanation that it was the hair that did the trick, of course was not correct. We know it was the lime, but no matter what

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his explanation was, his results measured in terms of finished leather were correct long before we chemists attempted to give him the right explanation for the phenomenon he observed.

The scientific investigators, in getting away from the practical side, have had several exceedingly interesting discussions on this subject, both here and in England, and as we have been doing a good deal of work in this field, we thought it might be interesting for you to hear what our experience has been.

There has been no question of the *one* function of the bating or puering process, *viz.*, the deliming. On that all authors agree and it is only with regard to the second function, *viz.*, the influence of the enzymes that discussion has arisen. Some like Wilson and Seymour-Jones claim that the chief, if not the sole, function of the enzyme is the digestion and removal of the elastin. Others like Rosenthal, Wood and Marriott take what we believe to be the sounder view, that while the effect of the bate on the elastin—be it digestion or some less far reaching effect—is undoubtedly one of its important functions, it is not yet established that it is the sole important or the primary function of the process; the essential effect of the bate on the elastin fibres is probably something considerably short of complete digestion, while there is every indication that a function of equal importance is the digestion and removal to some extent of the cementing or "interfibrillary substance." In trying to solve these questions two ways would suggest themselves, the one strictly chemical, to isolate the constituents of the skin as collagen, elastin, etc., before and after the bate to determine quantitatively what changes have taken place. After careful consideration we came to the conclusion that, at present, no sufficiently dependable methods of chemical analysis exist for our purpose. We therefore are compelled to resort to the histological methods which unfortunately do not give us quantitative results.

The histological part of the experiments hereinafter described were made in collaboration with the Department of Physiological Chemistry of Columbia University, and we are deeply indebted to Dr. Gies and his associates for the manner in which the work was carried out.

At the outset it appeared to us to be the logical procedure to begin our research on the bating of goatskins. As is well known

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these skins are very horny and hard natured and usually taken from a mature animal. To produce the necessary pliability in the leather and smoothness in the grain the skins are subjected to the beamhouse processes, soaking, liming, and bating, to a much more severe degree than practically any other type of skin. The skins are usually soaked for two to three days and these soaks are not always fresh and undoubtedly contain bacteria, which give rise to enzymes exerting some digestive action on the skins. From the soaks the skins go to the limes for about fourteen days and as a rule, depending of course on the nature of the skins, slightly over one-third of the time they are in old or mellow limes, which we know from other researches, to exert through their content of bacteria a digestive action of an order not far removed from that of a bate itself. After washing, comes the bating process. The skins, still fairly limy, are first given a short bate for two to three hours at a temperature of say 95° F. in an old spent bate made up and used the day previously. This old bate is usually rich in deliming substances including organic acids formed in the course of the bating process on the previous day. The skins, still slightly alkaline, are taken out and piled up on the floor, covered with skins flesh side out and allowed to stand two to three hours during which the liquor with which they are saturated from the old bate undoubtedly continues to act. A fresh bate is then made up, taking 10 per cent of dog manure or three-fourths of 1 per cent enzyme bate, calculated on the fleshed weight of the skins, and in this the skins are paddled for a short time at 95° to 100° F., temperature taken after the skins are put in. The paddles are then covered and left over night at approximately the same temperature. During this time the fermentation becomes very strong, the solution being at optimum temperature for the quick propagation of bacteria which generate both enzymes and gaseous products, which gradually float the skins until in the morning the skins are raised to the top and the temperature is about 7 to 8 degrees lower than the evening before. The skins show neutral in the cut and the liquor is faintly alkaline to phenolphthalein and smells strongly.

When this bating process is compared with that usually applied to calf skins—of which a brief description will be given later—or with the still milder bating of such leathers as harness or

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furniture leather, it will be appreciated why we considered it logical to examine first skins which had been bated with such a degree of severity that the effects of the bate would show with corresponding distinctness.

We were further of the opinion that if our conclusions were to be of value our experiments should duplicate commercial tannery conditions and that a laboratory experiment, even where the greatest care was taken to duplicate weights, temperatures and time does not fulfil this condition. Most tanners are familiar with the fact that they cannot always duplicate on a small scale results they obtain on a tannery scale. This is peculiarly the case with bating or any other process where fermentation plays a part. The reasons for this fact are very probably that the mass of skins and volume of liquor employed are so much greater, and also that the paddles are used for one and the same operation and for nothing else, so that the strains of bacteria carried from one batch over to the next are the same all the year round.

While artificial enzyme bates have successfully replaced the dung bates almost universally and while so far as can be ascertained their actions are fundamentally the same, we felt it was desirable to go back in our experiments to the original process of bating, *i. e.*, to the infusions of dog and chicken manure. Throughout our work, therefore, the manure bate is taken as the standard and parallel experiments are made with artificial bates.

We first arranged with one of our tanner friends to bate one regular pack of goatskins which had been limed as usual, with dog dung in the manner of old, and alongside of it a pack with artificial bate in their usual way. Skins were cut in half and one half bated with the dog manure pack and the other half with the artificial bate pack, in which case the procedure was as follows.

The skins were first run for two hours in an old bating liquor at 95° F. then thrown on the floor for three hours. Thereafter they were bated in a new liquor made up, in the case of dog manure with 10 per cent, in the case of enzyme bate with three-fourth per cent enzyme bate of the appropriate grade. In both cases skins were bated over night at 98° F. In the morning

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skins were raised and showed a practically neutral reaction to phenolphthalein, while the liquor itself was faintly alkaline to the same indicator.

Clippings were taken from corresponding points in each half after bating for histological examination and the skins subsequently finished into leather of the usual standard quality of this firm. The histological examination revealed that the elastin was by no means completely removed either in the case of the dog manure bate or the artificial bate.

This result was checked up in collaboration with another tanner using artificial bate (bating done exactly as described in the case of the previously mentioned experiment) from whose paddle clippings from skins chosen at random were taken. Strips about 2 inches by 1 inch were cut out of a number of skins about in the center and on the right-hand side of the backbone and preserved in dilute formaldehyde solution for histological examination. From another skin, pieces of equal size were cut from neck, belly, shank, flanks and butt, and also from the position already described. These samples were prepared in the generally accepted manner and microscopic sections were prepared and stained for examination. The skins, from which these clippings were taken, were finished along with the rest of the lot, as usual. There was a considerable amount of elastin present in all of the samples taken, no matter which part of the skin they were taken from. And all skins, when finished, gave normally good leather in every respect.

This finding was not unexpected; and led us to undertake a series of new experiments, in order to determine whether there is any difference between a dung bate employing bacterial enzymes or an artificial bate using pancreatic enzymes but with different types of delimers.

In this series of experiments the goatskins were taken from the tanner just after fleshing and washing and each skin was cut in half along the backbone. They were then numbered so that each skin gave two halves with identical numbers, showing the series, the batch and the individual skin number. The *right-hand* halves were all puered in an experimental paddle in exactly the same manner as in actual practice, employing an old bating liquor for two hours at 95° F. and then puering the skins

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over night at a temperature between 95° and 100° F. in a fresh bate prepared with three-fourth per cent of enzyme bate. Every day the bate of the preceding day was used first, then run to waste and a fresh bate of exactly the same composition prepared. The *left-hand* halves were treated in the same manner except that a dog dung bate was prepared from a fermented infusion of 10 per cent dog dung on the weight of the skins in the usual manner. Here too the old bate was used for primary bating on the next batch of skins, and then a fresh bate was prepared for overnight bating. The bate in all cases, both dung and artificial bates, worked normally and the skins were nicely raised the next morning and showed all signs of satisfactory working. The skins were then removed from the liquors, rinsed off and two complete skins, selected at random, were chosen. From each of these a small strip about 2 inches by 1 inch was cut from each half about 2 inches away from the tail and preserved in dilute formaldehyde solution for histological examination. The skins were then returned to the tanner and finished up together with the batch they were taken from, and gave leather of usual good quality.

We shall now endeavor to give you a description of what we saw. In every case the deliming was complete. The swelling had completely disappeared and the skins were absolutely normal in their fallen or flaccid condition. The finger print test was normal, and the porosity for air under pressure also, and no differences whatever were observed in this regard between artificial and dung bates. Naturally the skins bated with dung infusions, showed up darker as was to be expected. The results we show in our tables represent the average of a large number of sections taken from each skin. It is misleading to generalize from any single section as in any skin it is usually possible to obtain sections showing amounts of elastin varying over a wide range.

Series I in the accompanying Table I compares dog manure with enzyme bate, having beside the pancreatin preparation, ammonium chloride as a delimer; Series II, dog manure with enzyme bate, in which one kind of fermentable matter is used as a delimer; Series III, dog manure with enzyme bate, in which another kind of fermentable matter is used as delimer.

In the tables XXX means that approximately 50 per cent of the elastin is still present; smaller amounts are indicated by XX

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TABLE I.

Series No. I.—Goatskins

No. of specimen	Dog manure	Artificial bate No. 1
I-1-11	XXX (1)	XXX (2)
I-1-40	XX	X
I-2-7	XX	X
I-2-12	XX	XX
I-3-2	X	XX
I-1-20	0 (3)	X (4)
I-4-11	Trace	X
I-4-19	X	XX
"I-25-22"	0	Trace

Series No. II.—Goatskins

No. of specimen	Dog manure	Artificial bate No. 2
II-1-5	XX	XXX
II-2-15	X	XX
II-3-5	XXX (5)	XX (6)
II-4-5	XX	XXX
II-2-11	Trace	XX
II-1-17	Trace	XX
II-3-2	XX	XX
II-4-19	X	XXX

Series No. III —Goatskins

No. of specimen	Dog manure	Artificial bate No. 3
III-1-12	Trace	XX
III-2-13	X	XX
III-3-7	Trace	X
III-4-9	XX	XXX
III-1-17	X	XXX
III-2-7	XX	XX
III-3-5	X	X
III-4-10	XX	XX

and X and would approximate 25 per cent or 10 per cent respectively of elastin still present.

The comparison is always made with the amount of elastin normally present in original skin in the hair, as shown in Figures 10A and B. Figures 9A and B show sections after liming but before bating.

It would have made this paper too bulky to publish the photomicrographs of each section of skin tabulated in the table. A number of typical ones, therefore, were selected and are marked by numerals in parentheses in the table, which indicate the number of the photomicrographs herewith published.

Dr. Gies writes us in connection with these photomicrographs as follows:. . . . . "The photomicrographs forwarded to you are the finest illustrations of such skin sections that I have ever

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seen. You will be quite within the bounds of reasonable statement to say to those who examine them that they are quite exceptional in the clarity and distinctness with which they show the presence of elastin fibres." . . . . . "The A and B sections of the same numeral are vertical (A) and horizontal (B) sections of the same piece of skin. The B sections are through the planes in which most of the residual elastin fibres occur. The *heaviest black* lines—straight, waived or interwoven—are the reproductions of the elastin fibres. Fainter black impressions or gross black marks are *not* elastin fibres. In the original, the elastin fibres may be sharply identified by their *color* as differentially stained. . . . . I may add here that these histological examinations were carried on without any knowledge on the part of the histologist of what procedure these skin samples had been subjected to and, as a matter of fact, even corresponding halves were not examined together but at widely separated intervals. It would seem that the amount of elastin left is somewhat larger with enzyme bate than with dog manure, but compared individually this relation does not hold true strictly. This result corresponds with the relative enzyme strength of the dog manure bate and the artificial bate as measured. In this connection it must be observed that the strength of a dog manure bate cannot be controlled exactly. Temporary and local conditions such as temperature and the nature of the material will cause the bate to vary considerably either above or below the normal. The main thing to keep in mind is that the elastin is hardly anywhere completely removed, but the microscopic examinations show that the elastin layer has often been thoroughly broken up and the elastin fibres isolated and attacked, but it is very significant to see that the strong bates, that are used on goatskins to bring the grain down to the proper smoothness, are nowhere near sufficient to remove all of the elastin, although we should here under these circumstances rather expect to see such a result.

What has the puer actually accomplished beside the well known deliming action? It has brought down the swollen skin to a very soft, flabby condition; it has made the grain very smooth It has rendered the skin porous to air under pressure, and we see under the microscope that some elastin has been removed. From the histological observations we cannot generalize our conclusions

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because our staining method has only been used thus far to account specifically for the elastin fibres. We have not taken any other constituent of the skin under direct observation and consequently cannot estimate with any definiteness the relative importance of the changes which the elastin undergoes. However, we were able to draw the conclusion that so far as the elastin is concerned the effect of the bate is not so much one of digestion and removal as of loosening the elastin fibres from their moorings and fragmenting them.

Now let us look at the bating that is carried out on calf skins that require entirely different treatment although intended for essentially the same use as the goatskins, *viz.*, for upper leather. Calfskins are derived from a very young animal and the nature of the skin is soft and you might say liquid, compared to the horny, hard and tough goatskin. While we have in the goatskin the problem of bringing down the grain so low as to almost disappear and we solve the problem by depleting with a very strong enzyme bate, we find that the nature of calf-skin requires less depletion, *i. e.*, a weaker enzyme action, because here the grain is already smooth and the skin itself is softer. We may say, therefore, that goatskins and calfskins present more or less the two extremes of required enzyme action at least so far as skins for shoe leather are concerned. It will be therefore very important to see what happens on calfskins.

Here too we followed exactly the conditions actually obtaining in the manufacture of calf leather. Most of the calfskin tanners in this country use what is called a running bate, *i. e.*, they use the same bate continuously, strengthening it up with fresh bate before each pack is entered, and occasionally running off some of it if the bate gets too putrid. In the old days 3 per cent of chicken manure on the fleshed weight of the skins was soaked over night in warm water and then an infusion was made of it to be added to the bate before entering the skins. Now-a-days from one-third to three-fourth per cent of enzyme bate of the correct grade is added directly to the bate. After entering the skins, the temperature was maintained at about 85° F. with occasional paddling, the skins were treated in it for 2 to 3 hours until the grain felt very smooth and the skins had fallen to a nice soft

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flaccid condition, but not too much so. Our bating experiments on calfskins were conducted as follows.

The skins were received in the morning after they had been fleshed and washed. They were then cut in halves and numbered as already shown. The *left-hand* sides were treated in an infusion of chicken manure and the *right-hand* halves in enzyme bate at 85° F. The treatment was continued at this temperature only so long as was deemed necessary to give the skins the right qualities of a bated skin and this took usually from 2 to 3 hours. You see in this case we have comparatively weak enzyme action

TABLE II.

Series No. IV.*—Calfskins		
No. of specimen	Chicken manure	Artificial bate No. 4
IV-1-6	XX	XX
IV-1-7	XX	XX
IV-2-3	XX	XX
IV-2-5	XX	XX
IV-3-5	XX	XX
IV-3-9	XXX (7)	XX (8)
IV-4-2	XXX	XX
IV-4-10	XXX	XXX

Series No. V.*—Calfskins		
No. of specimen	Chicken manure	Artificial bate No. 5
V-1-1	XXX	XX
V-2-3	XXX	X
V-3-5	XX	XX
V-3-10	XXX	XX
V-4-8	XX	XX
V-1-4	XX	XX
V-2-9	XX	XXX
V-4-1	XX	XX

*Series IV and V again differ only in the nature of delimer accompanying the pancreatic enzyme preparation.

over a very short time while in goatskin manufacture we have comparatively strong enzymes over a long period. When the skins were "down" enough, they were removed and rinsed off and clippings were taken in the same manner as previously described. The bating liquor was then brought to 85° F. again and kept at that temperature over night. Before they were used again, the bates were freshened up on the second day with an infusion of 2 per cent chicken manure and three-fourth per cent of enzyme bate respectively; the third day with 1½ per cent chicken manure and one-half per cent enzyme bate; and the fourth day with 1 per cent chicken manure and one-third per cent of enzyme bate respectively. The skins, after bating was completed, usually showed themselves faintly alkaline to phenolphthalein, especially

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in the thicker parts—as is universally the case in practice. After rinsing off, the skins were pickled with 100 per cent of water, 1½ per cent sulphuric acid and 12½ per cent of salt and were then returned to the tanner, where they were worked up together with the same batch they were taken from and gave leather of the usual high grade.

The histological findings of these experiments are given in Table II. The amount of elastin still present is considerable and does not vary greatly between the enzyme bate and chicken manure series. I am afraid that, if we had endeavored to remove all of the elastin, especially in these calfskins, we would have experienced trouble in the form of loose leather or at least a considerable pipiness of the finished leather. It would seem that this latter fault in leather may be produced by the removal of those fibres that hold the grain layer fastened to the corium. Of course this fault would be greatly minimized by using a vegetable tannin, which gives more body to, and fills the skins more than the usual chrome tanning process does.

There is one observation which applies to our findings in the case of both calfskins and goatskins which might be made at this stage. We have compared the condition of the elastin fibres after bating with their condition "in the hair." It is more than probable that an action similar to that of the bate is exerted by the soaks and limes particularly where these are mellow—and the extent to which the elastin fibres may be broken from their connections and fragmented as well as even digested in these is an interesting problem on which we may later be able to throw some light.

The histological findings in all of these cases presented to you confirm to a very large degree the work of Marriott, but differ in some respects from the conclusions come to by Seymour-Jones and Wilson.

It remains to be seen if there is any other action going on, due to the presence of enzymes, that has not yet been made visible under the microscope. I imagine that the substance, usually referred to as "interfibrillary substance" is distributed as an unformed jelly or viscous liquid between the fibres of the skin and subject to changes in every step of the manufacturing process in

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the beamhouse. It would be interesting to know how the interfibrillary substance behaves and how much interfibrillary substance there is in the freshly flayed skin; in the skin as it is preserved by salting or drying; how much of it dries out in this stage and becomes soluble or irreversible; and how it is acted upon by the soaking and liming before it is subjected to the bating action.

From the point of view of the practical tanner there seems to be little doubt that the removal of such interfibrillary substance, what is generally described as scud, *does* constitute one of the most important functions of the bating process. This phenomenon of the scud flowing out from the skin has not received as much attention as we should wish, and as seems to be indicated by the very necessity of the operation in the actual manufacture of leather. As an example may be taken the bating of lamb skins in the manufacture of glove leather. If the attempt is made to scud these before bating, the scud adheres to the knife in the form of a substance of cheese-like consistency, whereas when scudding is conducted after bating, the scud flows freely from the skin in a liquified form, in a consistency only little greater than that of water.

From the histological standpoint I imagine that the scientific explanation of the bating operation and of this scud will present quite a few difficulties, since to my knowledge no selective stain has been found for the probably very heterogenous mixture constituting the cementing substance or interfibrillary substance.

My advice to all workers in this interesting field would be to see first through the eyes of the practical man and not to neglect the close observation of all small details. This matter of scud flowing out from the skin may prove to be the most important function of the bate after all.

While running these comparative experiments with manure bates and enzyme bates, we have taken at regular intervals samples of the bating liquor and have determined the enzyme strength. Some very interesting observations have been made in this manner and we propose to publish the results in a future paper.

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Figure 1 A

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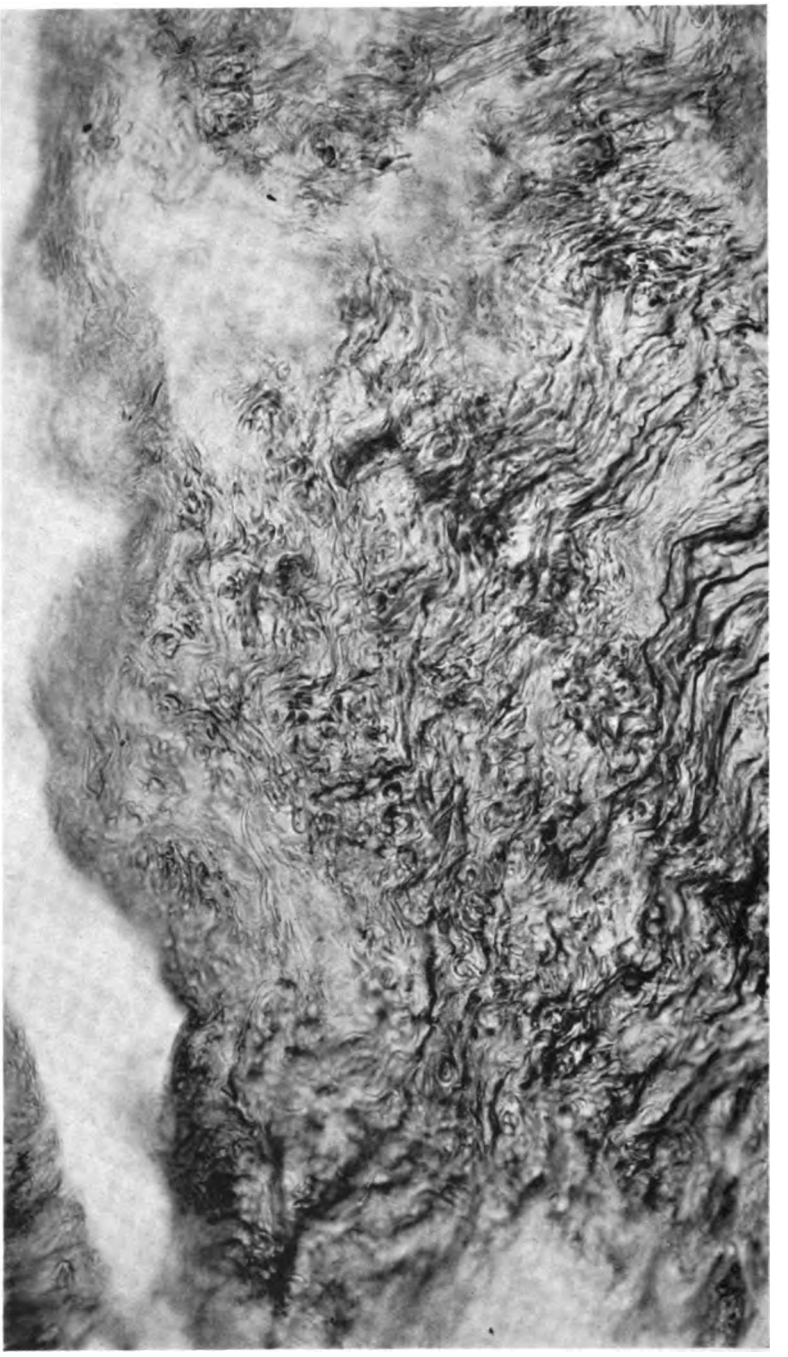

Figure 2 A

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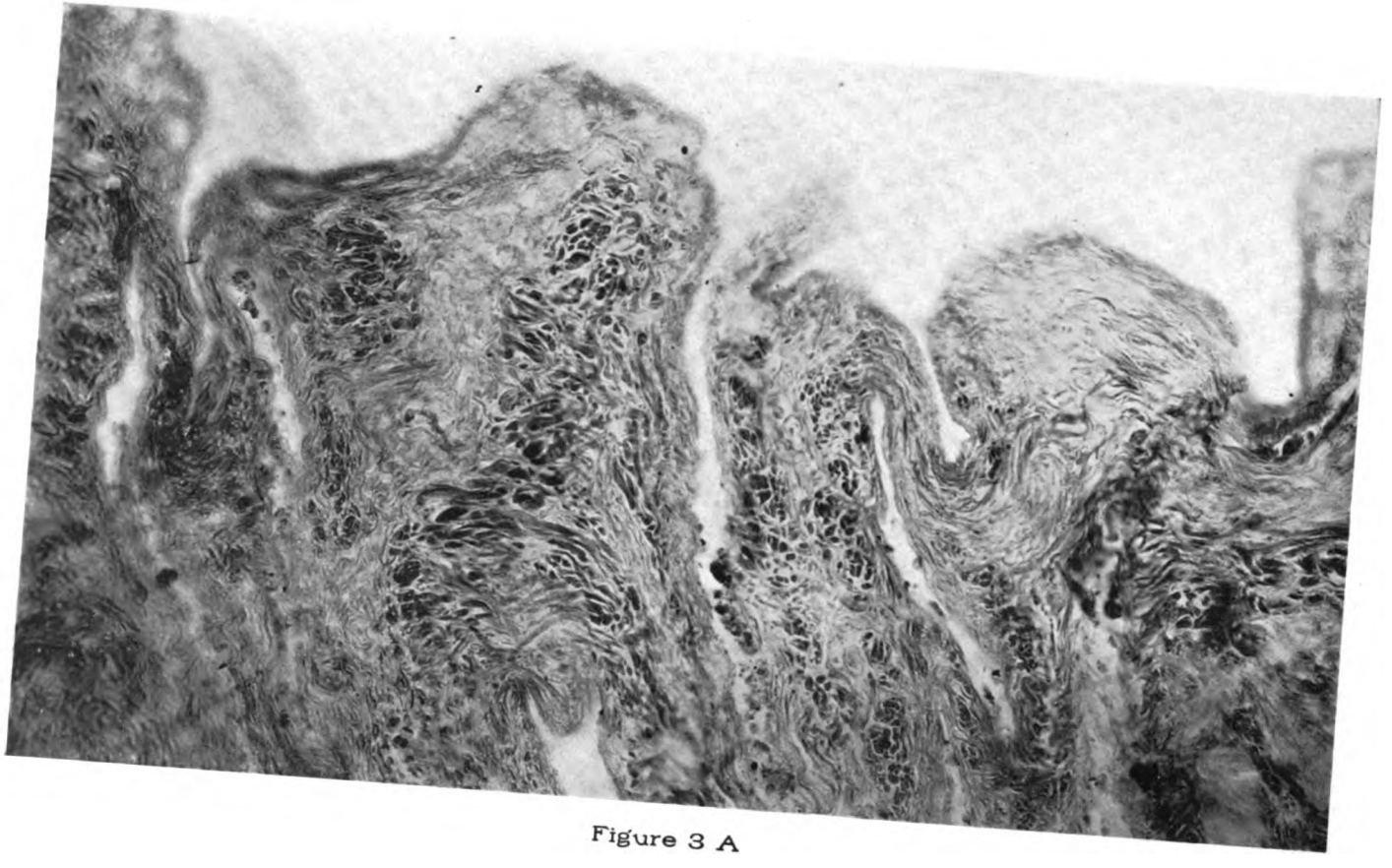

Figure 3 A

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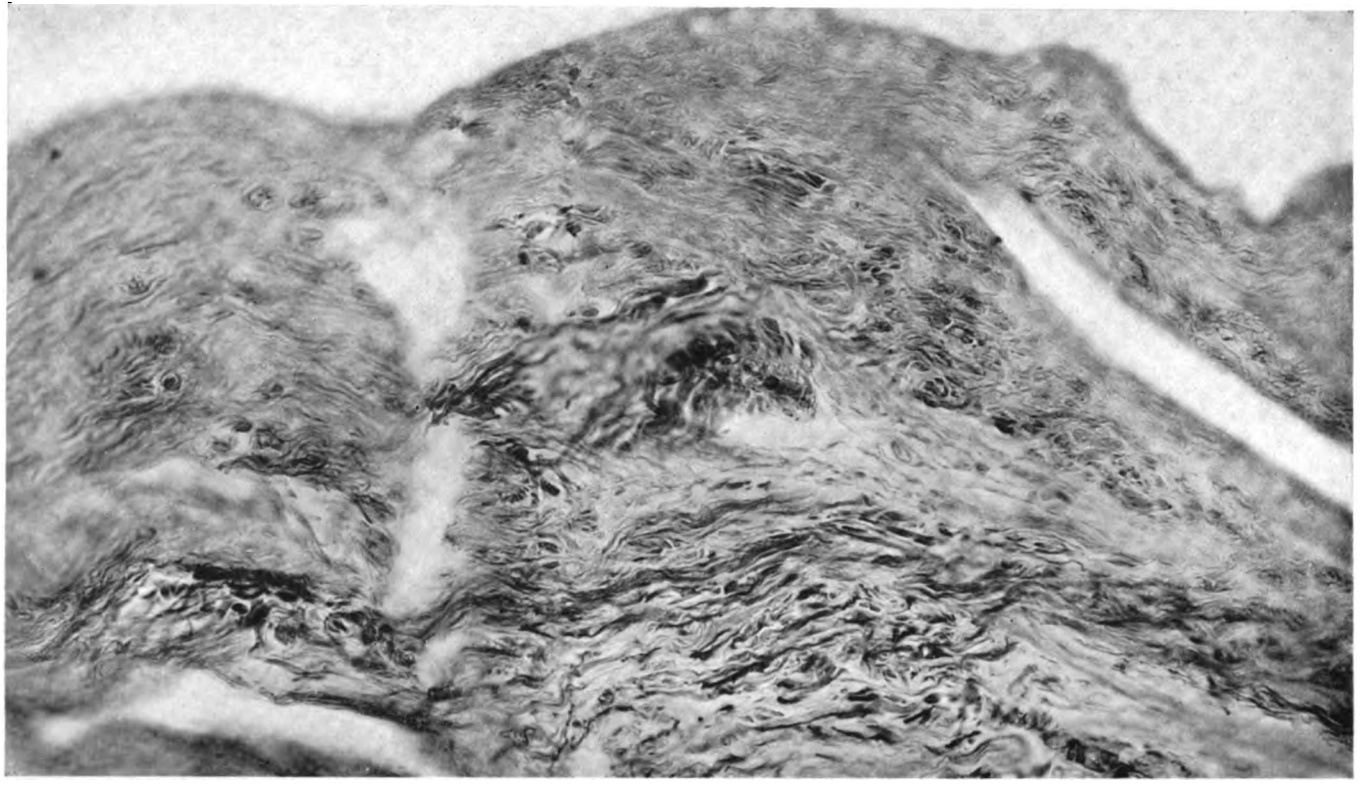

Figure 4 A

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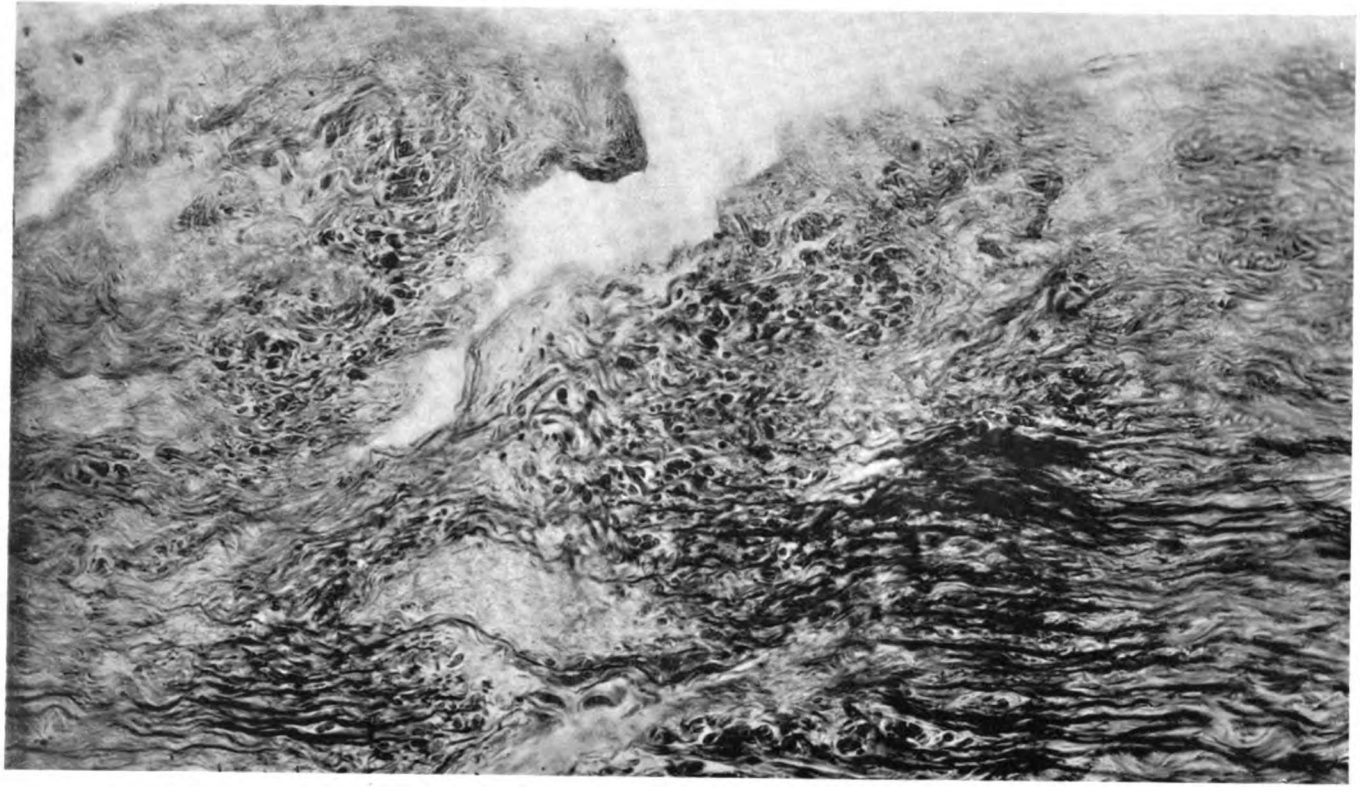

Figure 5 A

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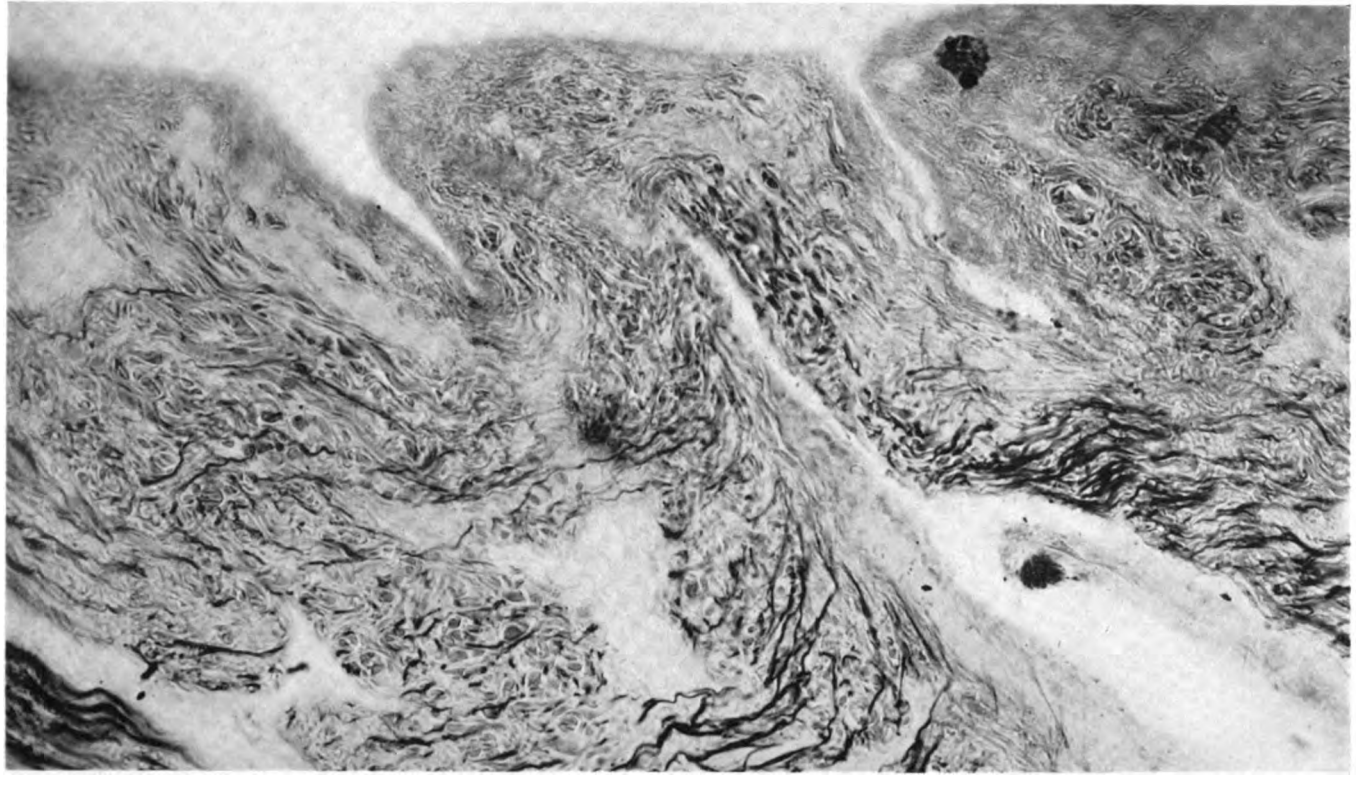

Figure 6 A

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Figure 7 A

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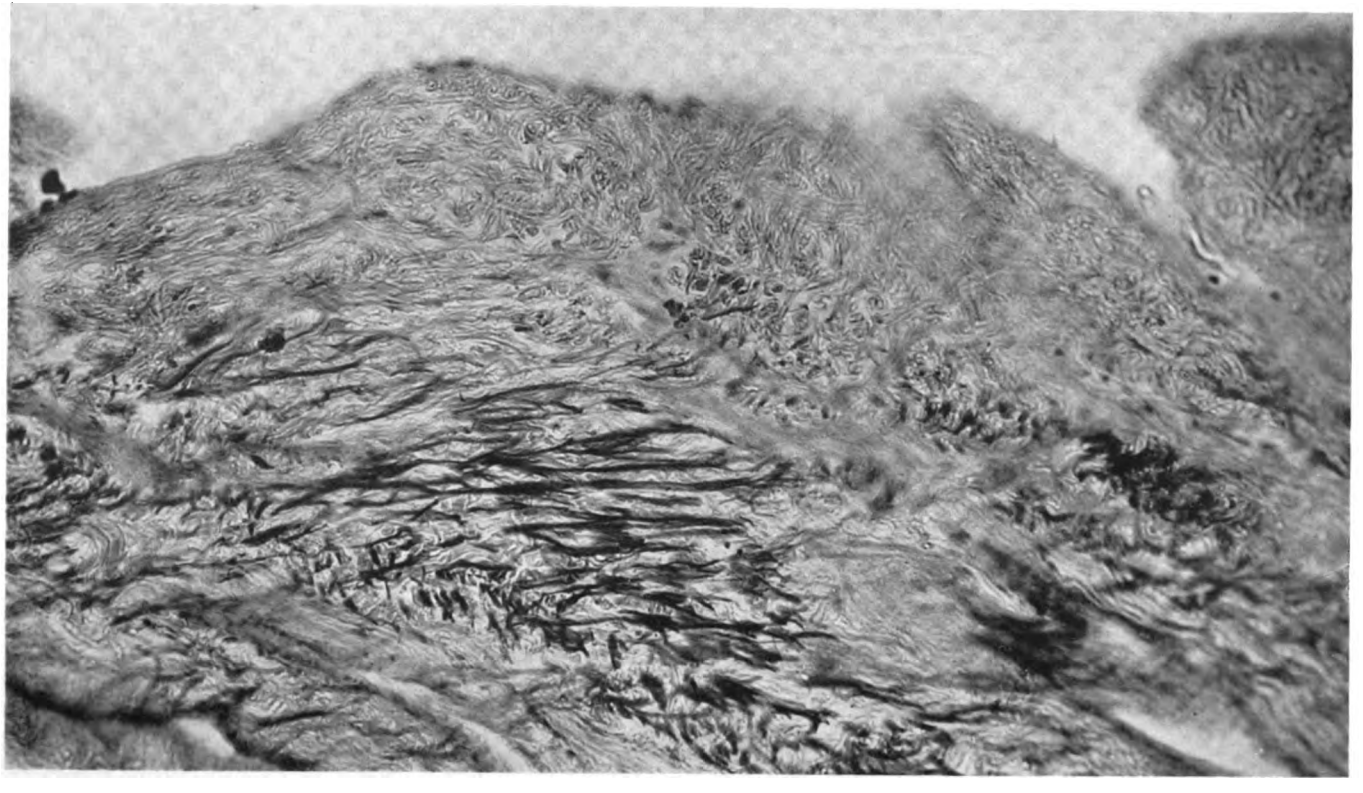

Figure 8 A

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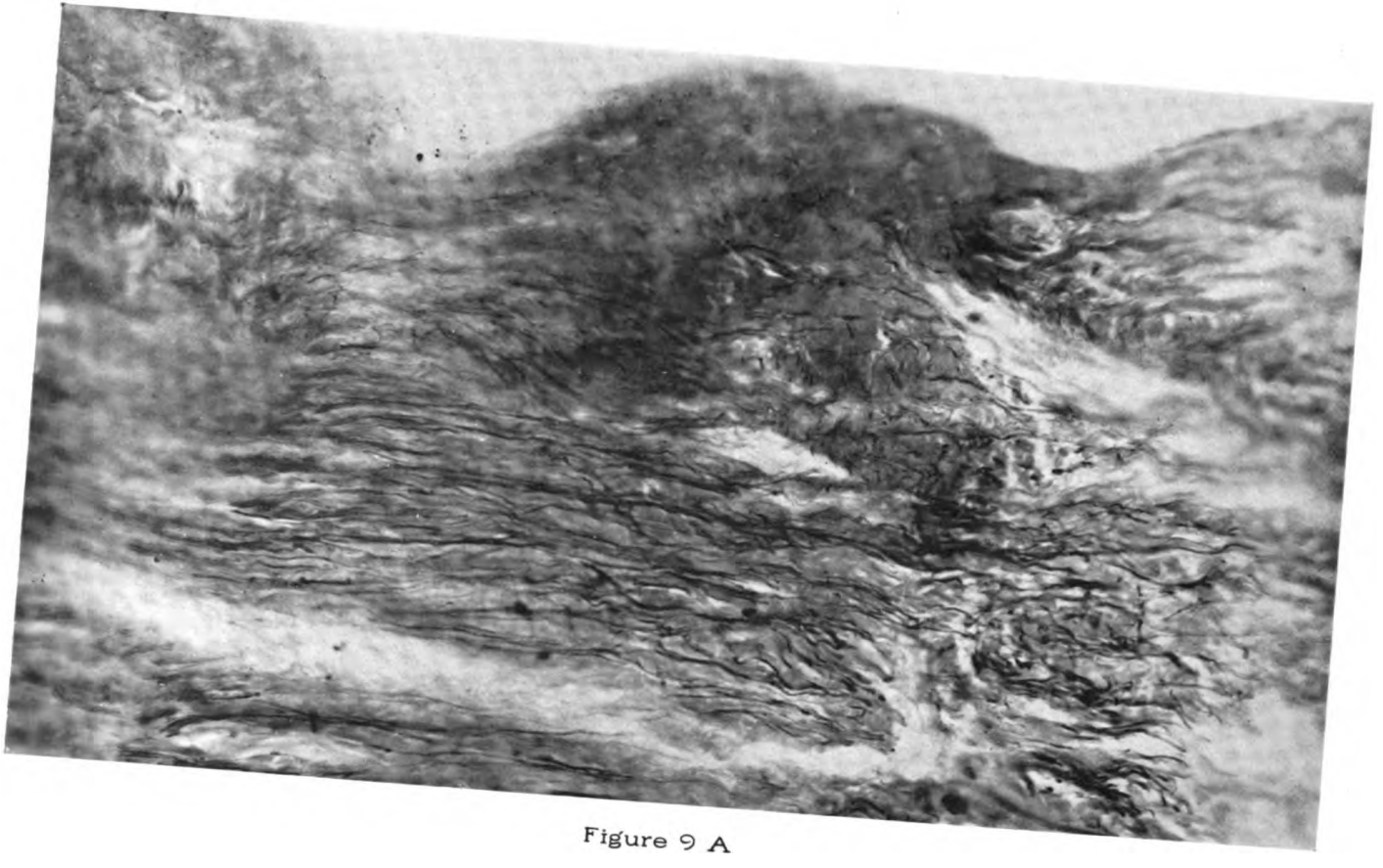

Figure 9 A

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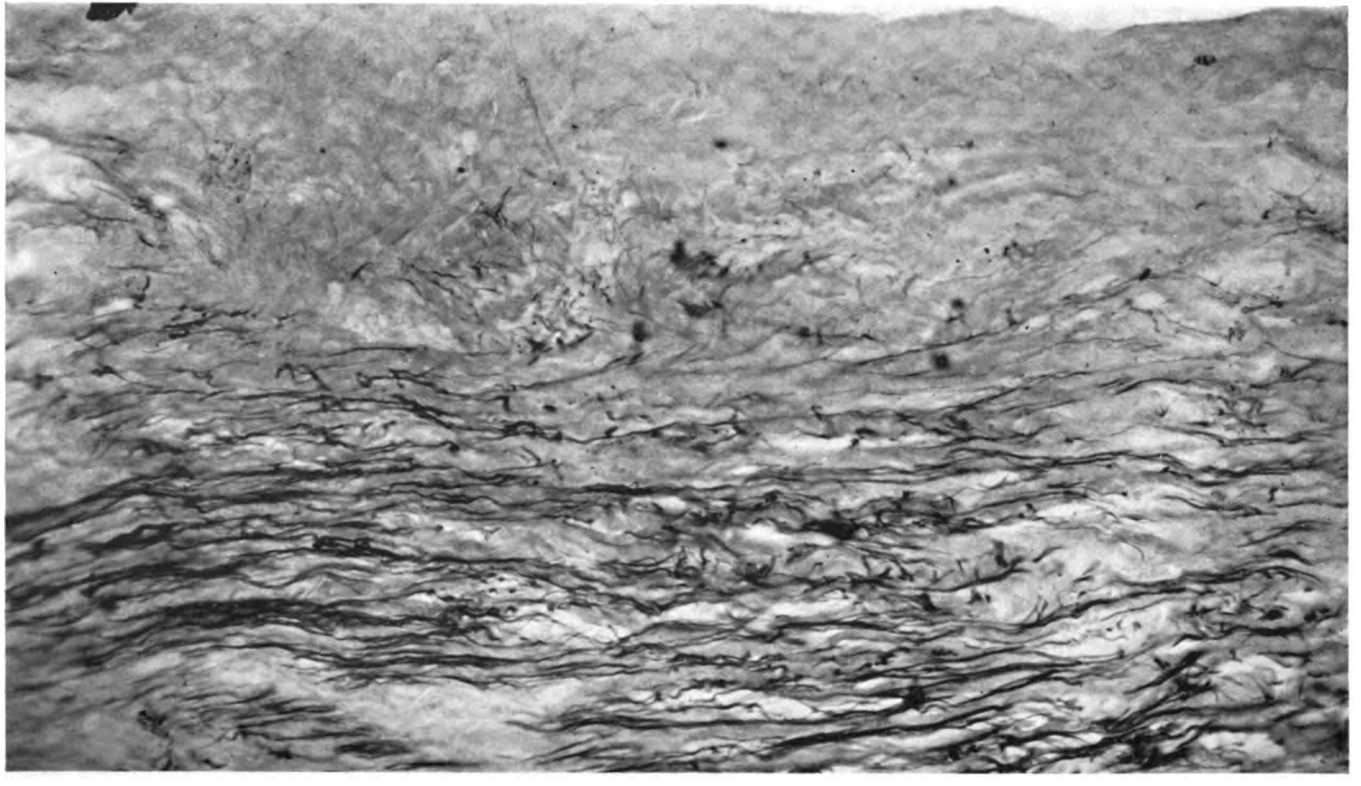

Figure 9 A_2

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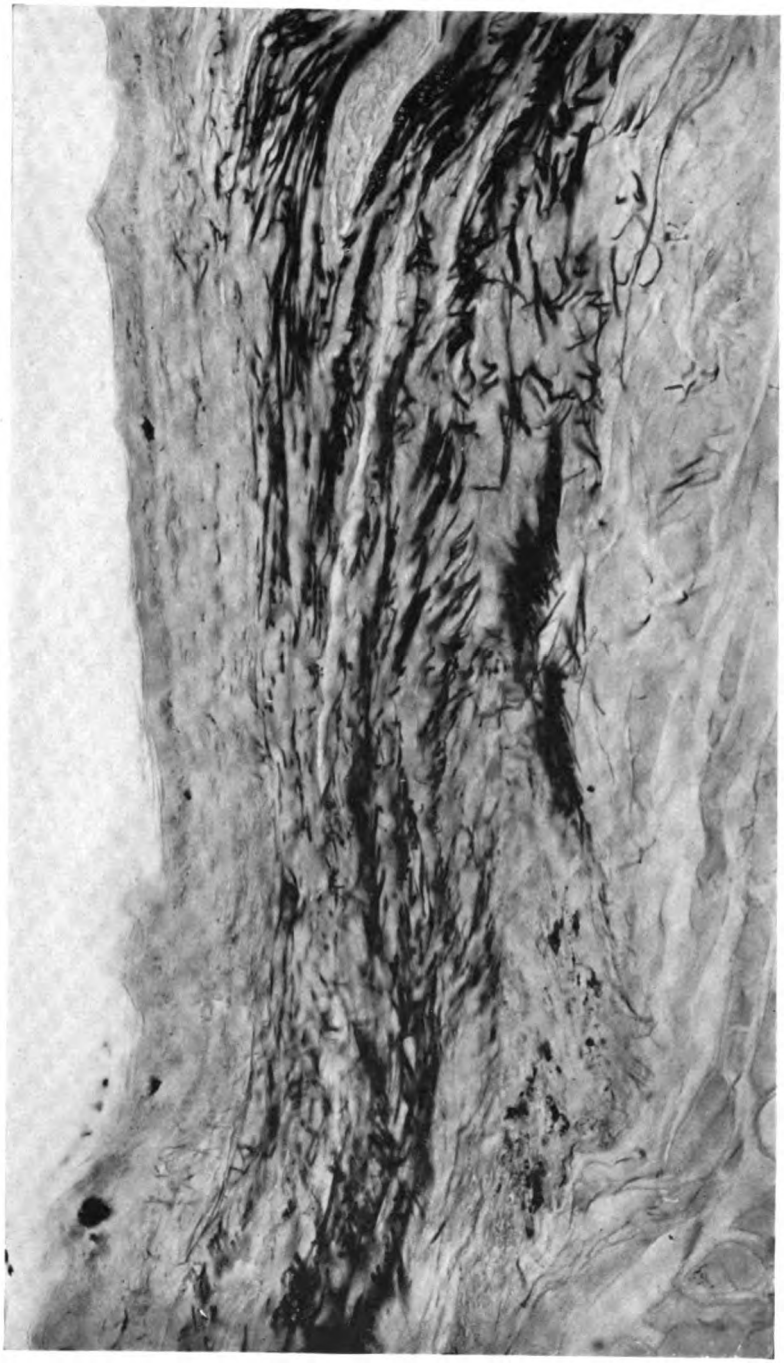

Figure 10 A

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Figure 1 B

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Figure 2 B

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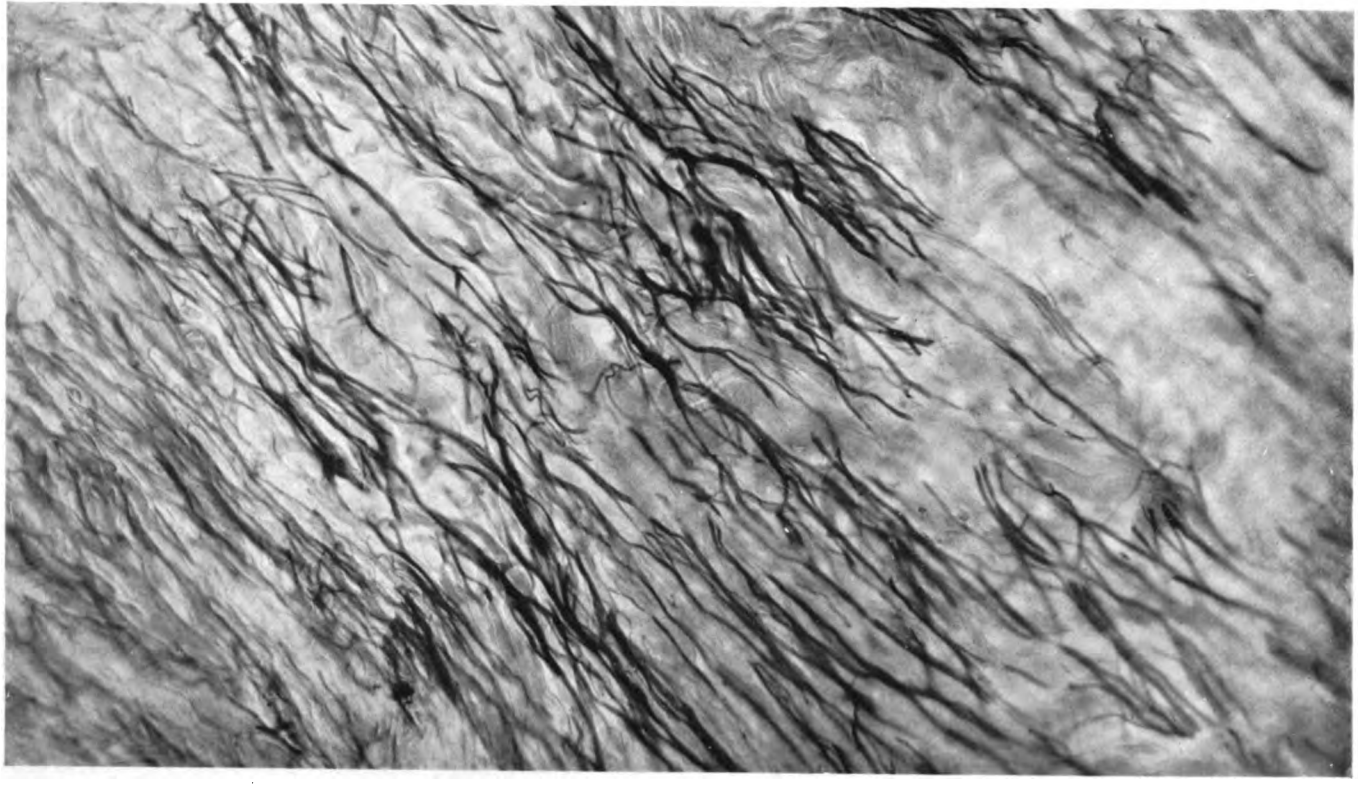

Figure 4 B

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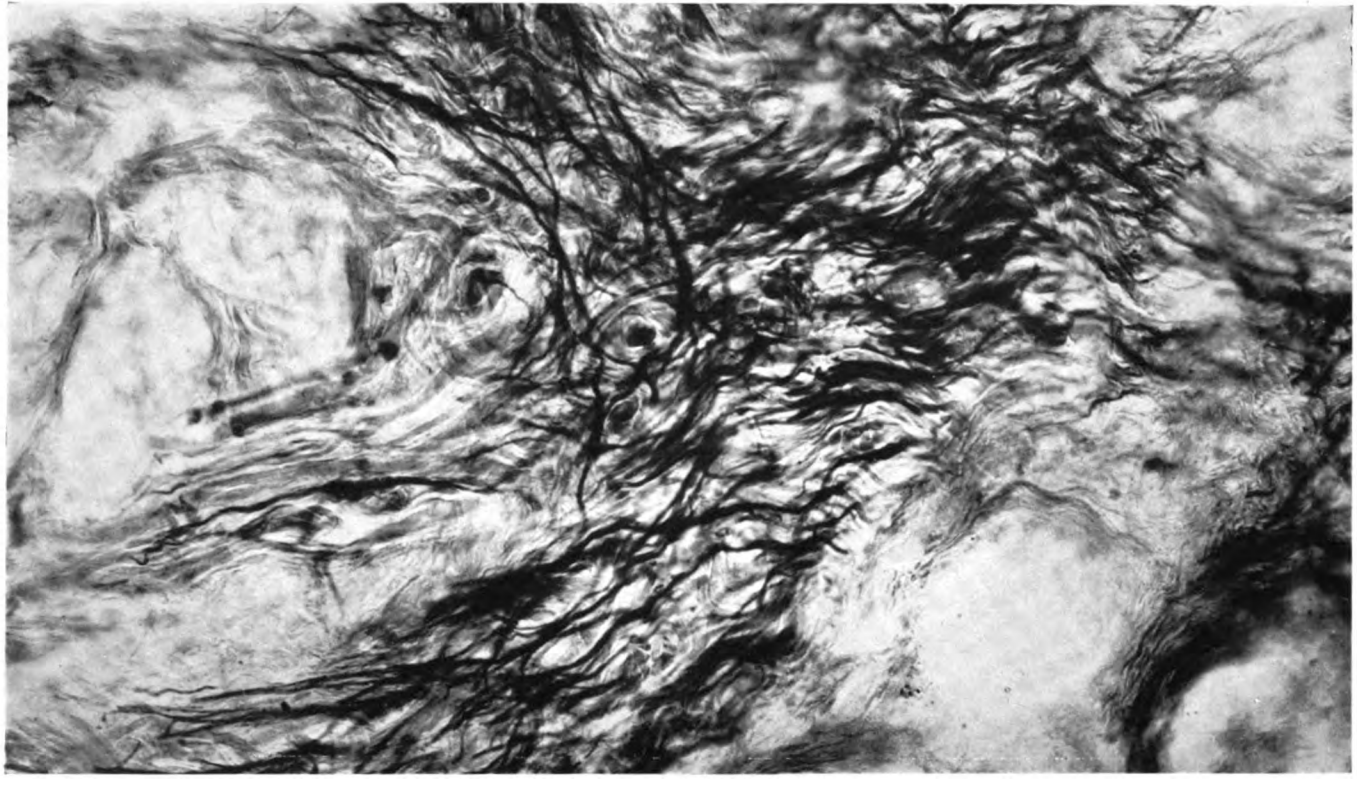

Figu re 5 B

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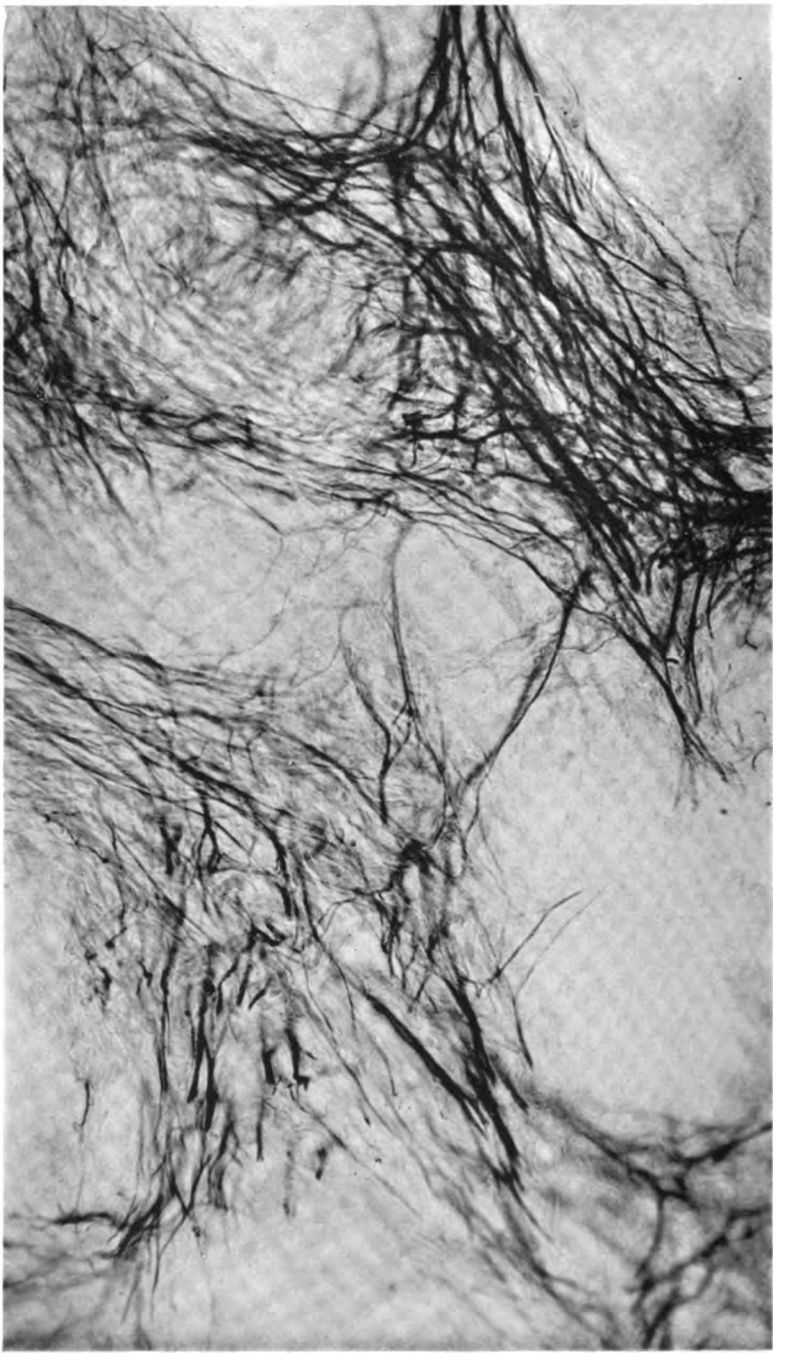

Figure 6 B

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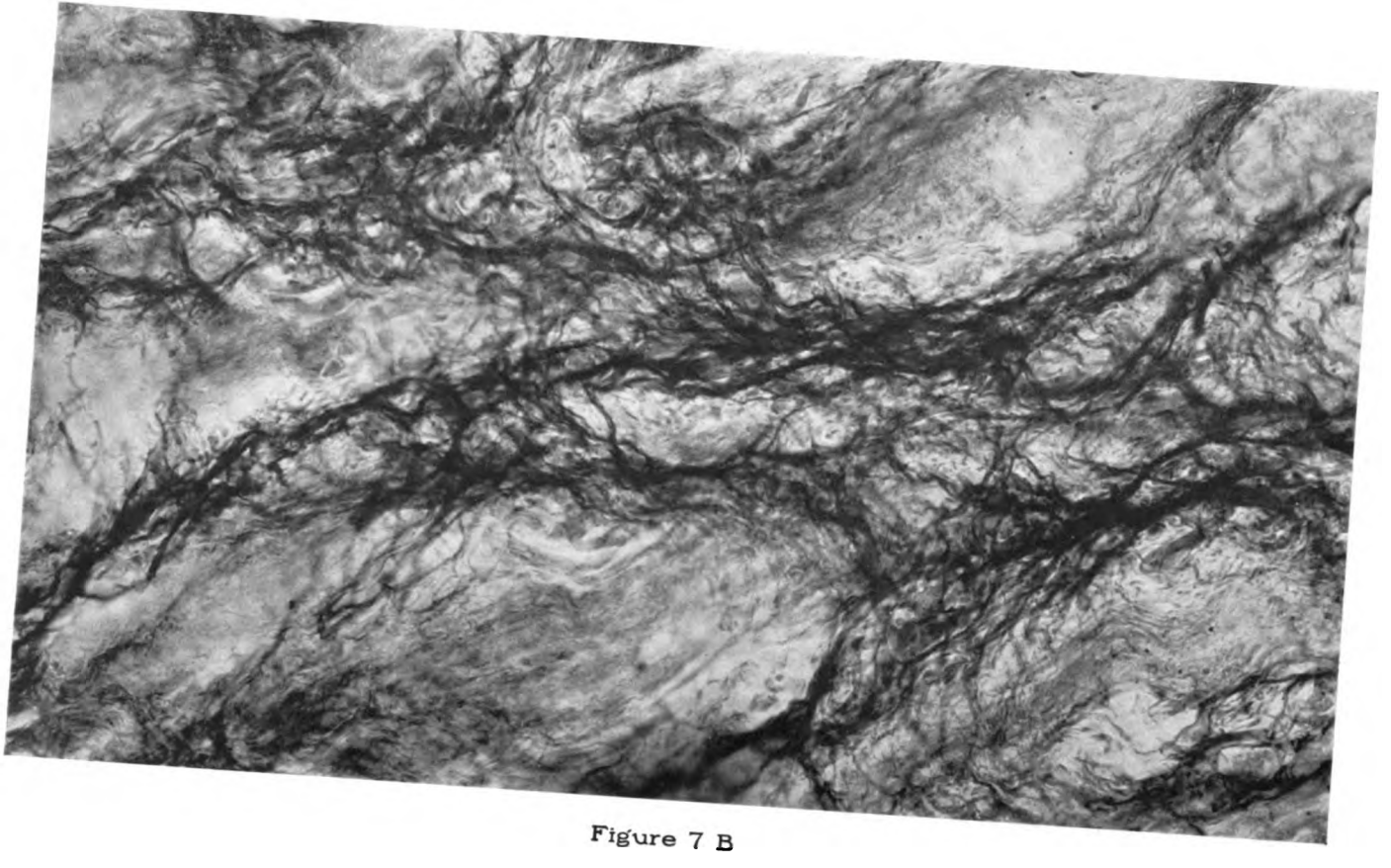

Figure 7 B

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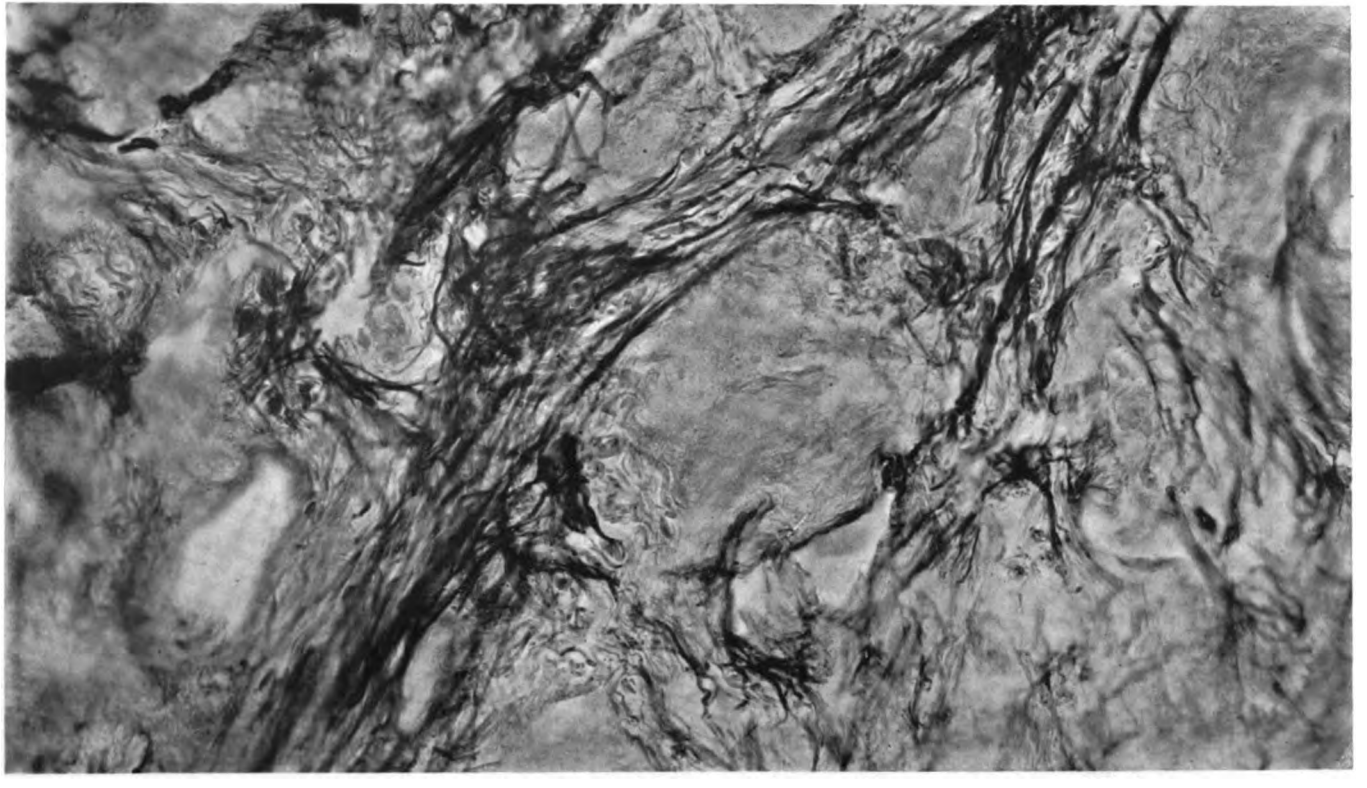

Figure 8 B

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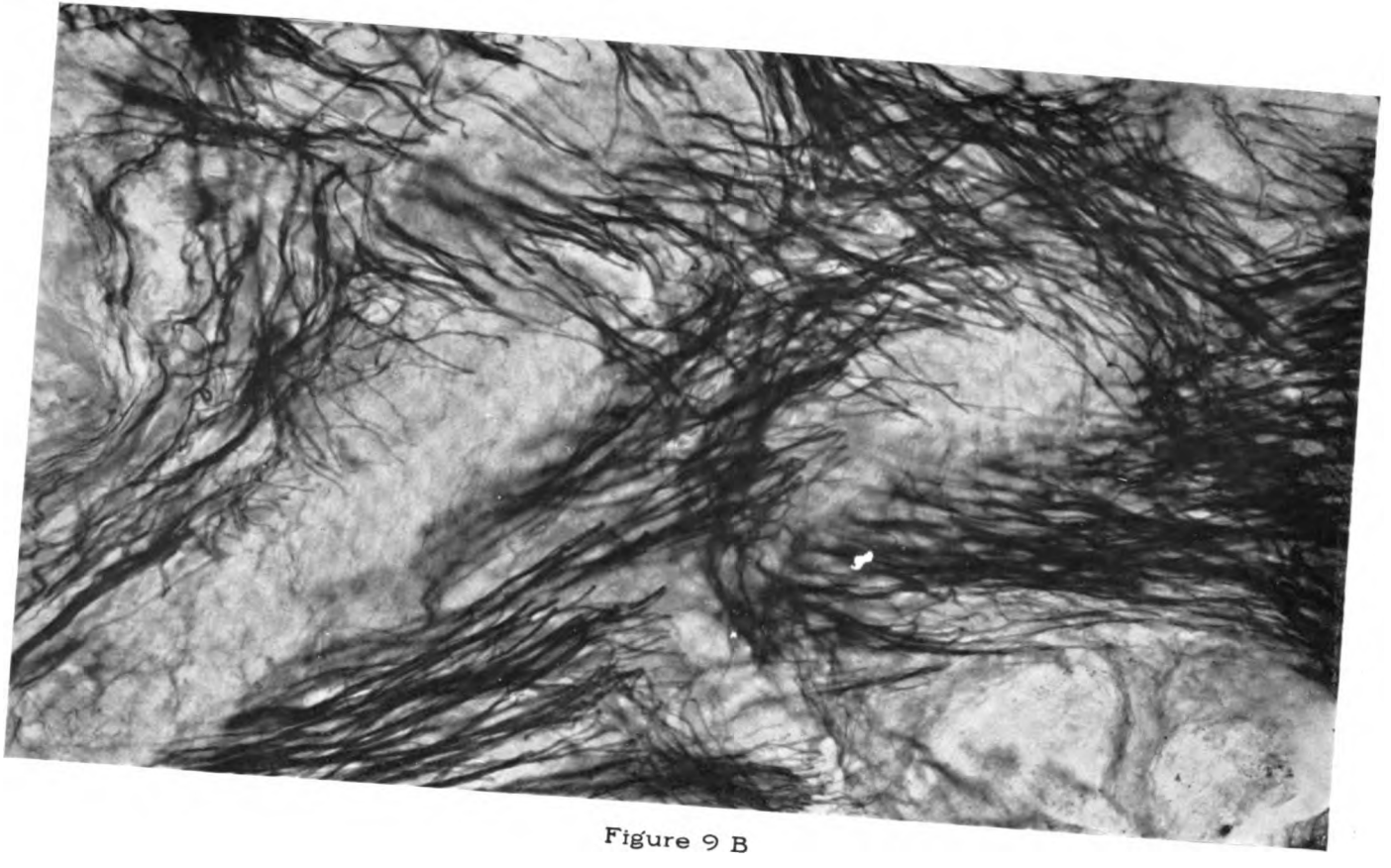

Figure 9 B

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Figure 10 B

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MODERN PROBLEMS IN CHROME TANNING*

*By Donald Burton***

Much has been accomplished since the chrome tanning industry was first started by the employment of chrome compounds as tanning materials in 1884, when Augustus Schultz of New York was granted a patent for his "improved process for the tawing of hides and skins, and Martin Dennis of Newark placed his basic chromium chloride liquor on the market in 1893. The many difficulties with which the commercial development of the process has been attended have been gradually overcome by the co-operation of the initiative of the tanners, the enthusiasm of the leather chemists, and the utilization of labor-saving machinery. More particularly in recent years the knowledge which has resulted from the research, which Professor Procter commenced as far back as 1897, has opened up new fields of enquiry which are doing much to elucidate the principles which underlie the process.

In view of the part which America has played in founding and advancing this important industry, it seems not inappropriate to consider the problems which confront the tanner at the present time in this Conference. In order to realize these it will be well to start at the limeyard for, on account of the empty nature of the tannage, defects show up more with chrome than with vegetable leather, and it is therefore necessary to effect a quick liming with little loss of hide-substance to avoid a loose leather and minimize the tendency to stretch. With regard to the actual tannage many factors have to be considered and it is more especially with regard to a proper utilization of these that the chrome tanner can look forward to improvements in the efficiency and cost of his process. It is becoming more and more evident that the chrome content and basicity are not in themselves a sufficient guide to the tanning properties of a liquor. The influence of the former is to a large extent dependent on the presence of other substances such as gum-tragasol in the liquor, while the latter is deficient as a means of control in several very important aspects.

* Read at the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Ontario, Canada, June 22, 1922.

** Head of the Leather Section, C. W. S. Research Department, Manchester, England.

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The basicity, as determined by the present official methods, takes no account of volatile acids like carbon dioxide and sulphur dioxide. When chrome liquors are manufactured by adding soda ash to chrome alum the acid present reacts with this liberating carbon dioxide according to the equation:

$$H_2SO_4 + Na_2CO_3 = Na_2SO_4 + H_2O + CO_2.$$

It has been shown by experiments with green and violet chrome alum solutions[1] that this liberated carbon dioxide functions as an acid, and therefore more alkali is necessary to bring the solution to the precipitation point. This has been further demonstrated by ascertaining the amount of caustic soda required to start precipitation in a solution of chrome alum, and adding a slight excess. On passing washed carbon dioxide through the solution the turbidity will be seen to disappear. The importance of this will be realized in tanneries where the liquor is neutralized in the later stages of tanning by the addition of quantities of washing soda, or soda ash, obtained by a calculation which neglects the effect of this liberated carbon dioxide. Hence Harvey[2] and the author[3] have independently suggested that greater accuracy would be obtained by addition of alkali before boiling in the determination of the acidity, and this has been confirmed by the author in collaboration with Mr. Hey.[4]

The basicity however fails as a means of control much more seriously in other directions. This, expressed in the European fashion as the amount of SO_4 associated with fifty-two parts of chromium, is obviously a measure of the total acid present in a liquor, and gives no indication of the concentration of the free or hydrolyzed acid which is one of the factors controlling chrome tannage. Indeed it has been shown that liquor of the same chrome concentration, basicity figure and even neutral salt content may have entirely different tanning properties. The condition of the fibre when it is fixed by the chrome is of fundamental importance in determining the properties of the leather. It is well known that pelt tanned in a fallen state tends to be soft and pliable, but in the swollen condition it is hard and firm. Hence the degree

[1] Chrome Tanning. I., *J. S. L. T. C.*, 1920, 205.

[2] Practical Leather Chemistry, page 56.

[3] *J. S. L. T. C.*, 1920, 207.

[4] The Determination of the Basicity Figure of One-Bath Chrome Liquors, *J. S. L. T. C.*, 1920, 272.

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of swelling produced by a chrome liquor must be regarded as one of the first essentials in ascertaining its tanning properties.

The problem of the determination of the acidity of a chrome liquor is one therefore which merits attention and has been discussed fully in a previous communication,[5] but perhaps some rather interesting results obtained by one of the proposed methods may be given here. Since the rate of hydrolysis of chrome salts is generally supposed to be low it was thought that possibly the free hydrolzed acid in a chrome liquor might be measured by the liberation of iodine from a mixture of potassium iodide and potassium iodate according to the equation:

$$3H_2SO_4 + 5KI + KIO_3 = 3I_2 + 3K_2SO_4 + 3H_2O.$$

A solution of pure chrome alum was prepared by dissolving 50 grams in a litre of cold water. Five hundred cc. of this solution was boiled for half an hour, cooled and made up to the original volume. From the following equations it will be seen that one cc. of N/10 NaOH is equivalent to one cc. N/10 $Na_2S_2O_3$:

$$3H_2SO_4 + 5KI + KIO_3 = 3I_2 + 3K_2SO_4 + 3H_2O$$
$$3I_2 + 6Na_2S_2O_3 = 6NaI + 3Na_2S_4O_6.$$

Preliminary experiments showed that the further hydrolysis proceeds at a very much more rapid rate than is usually thought to be the case, and the following procedure was found to be necessary: Twenty-five cc. of the chrome alum was pipetted into a flask, a little starch solution and a mixture of 10 cc. of a 10 per cent solution of potassium iodide and 25 cc. of a 2 per cent

TABLE I.

Solution	Cc. N 10 thiosulphate
Green	20.75
Green	20.45
Green	20.25
Theoretical (calcd. from Blockey's results, *J. A. L. C. A.*, 1918, 573)	5.1
Violet	17.1
Violet	17.2
Theoretical (calcd. from Blockey's results)	0.3
Violet + excess Na_2SO_4	11.4

[5] The Relation between the Properties of Chrome Liquors and the Leather they Produce. Some Notes on the Mechanism of Chrome Tanning with Bibliography, *J. S. L. T. C.*, 1922, 155.

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solution of potassium iodate quickly added. The thiosulphate was run in as rapidly as possible from a burette and the point at which the blue color of the starch was *momentarily* discharged taken as the end-point. The results are given in Table I.

These results show that the hydrolysis of chrome salts proceeds very rapidly when the free acid is removed from the solution by alkali or hide-substance, but this will be slower in the case of basic chrome liquors than with chrome alum solutions.

In view of these results it would only seem possible to determine the free acidity by some method which would not disturb the equilibrium such as the electrometric, but in any case a determination of this quantity would not furnish an effective means of control, for its influence is modified by the presence of other bodies in the liquor. Furthermore, it is not enough to know how much acid exists, or can be formed, in the liquor without taking into account the relative amounts of this and the pelt. Obviously the greater the quantity of pelt present in a given liquor the more acid will it abstract, and hence this will have the effect of making the liquor function as being more basic.

The properties of a liquor are still further affected by the presence of other substances such as neutral salts, sulphur, excess of reducer where they have been prepared from bichromate by reduction with either SO_2 or any organic substances such as glucose, flour, starch, whey or spent tanning materials.

The modern study of the Neutral Salt Effect may be said to result from a discussion started by Dr. Klaber, at your Annual Meeting in 1917, to ascertain why the addition of salt makes possible the use of more basic chrome liquors and much work has been carried out since, in this connection, both in America and England.

The writer conceived the idea[6] that the Neutral Salt Effect was due to the equilibrium resulting from the interaction of the hydrolyzed acid in a chrome liquor with the added salt as represented by the following equations (where M may be either K, Na, NH_4, Mg, etc.):

[6] A Further Aspect of the Neutral Salt Effect, *J. S. L. T. C.*, 1921, 192.

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Basic chrome salt + $H_2O \rightleftarrows$ More basic chrome salt + H_2SO_4.

$$\left.\begin{array}{l} H_2SO_4 + MCl \rightleftarrows MHSO_4 + HCl \\ MHSO_4 + MCl \rightleftarrows M_2SO_4 + HCl \end{array}\right\}$$

$$H_2SO_4 + M_2SO_4 \rightleftarrows 2MHSO_4.$$

Since free acid is consumed in the formation of the acid sulphates it follows that the addition of neutral salts will give rise to more basic chrome salts in the liquor, but sulphates will have a greater effect than chlorides since HCl is produced in the case of the latter. The retardation of the penetration of the chrome found by Wilson and Gallun[7] and also by the author and Mr. Glover is in agreement with this hypothesis.

The neutral salt will however affect not only the chrome penetration but also the acidity of the pelt and it has been shown by the author in collaboration with Mr. Glover[8] that this is increased by chlorides and decreased to a greater extent by equivalent quantities of sulphates. In compiling a bibliography of the chrome tanning industry recently, the author came across a paper[9] published by Proctor and Griffith in 1900 which seems to have been entirely overlooked. The experimental results in that paper are in agreement with those described above, and it may therefore be taken that this point is established, though experiments on the effect of neutral chlorides and sulphates in gradually increasing concentrations are still necessary. In this department considerable work has been done in connection with a new method for determining the acidities of chrome liquors in order to accomplish this more easily. If a neutral oxidizing agent be used for the oxidation of a chrome liquor, containing a known excess of caustic soda, the diminution in alkalinity should be due to that consumed in neutralizing the acidity of the liquor and that used in forming sodium chromate. By calculating the latter from the chromium figure, the former should be obtained by difference. A method has been worked out in conjunction with Messrs. A. Glover and R. P. Wood in which hydrogen peroxide is used as the oxidizing agent. This has been shown to yield accurate and concordant results with pure chrome solutions[10] but its application

[7] The Retardation of Chrome Tanning by Neutral Salts, *J. A. L. C. A.*, 1920, 273.
[8] The Influence of Neutral Salts on the Progress of Tannage, *J. S. L. T. C.*, 1922, 6.
[9] The Absorption of Basic Chrome Salts by Skin, *J. A. L. C. A.*, 1917, 612.
[10] A New Method for the Determination of the Basicity Figures of Chrome Liquors, *J. S. L. T. C.*, 1922, 92.

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to liquors containing dissolved hide-substance and organic bodies is still under investigation.

We are now in a position to study the swelling power of a chrome liquor. This is dependent on the following four factors:

I. The Free Acidity.
II. The Neutral Salt Content.
III. The Relative Rates of Absorption of Acid and Further Hydrolysis of the Chrome Salt.
IV. The Relative Rates of Absorption of Acid and Fixation of the Grain by the Chrome.

In most chrome liquors we are dealing with the descending portion of the swelling curve and it therefore follows that the swelling will diminish as the acid increases in concentration. The effect produced by the addition of a neutral chloride will be the sum of two forces acting in the same direction. The swelling will decrease with the increase in acidity which has been shown to result from the addition of neutral chlorides[11] and the latter will exert a dehydrating influence and repress the swelling. Thus a softer and more pliable leather will be produced unless too much chloride be added when the repressive action will become too great and there will be a tendency to flatness. The light color and nice grain is due to a preliminary pickling produced by the hydrochloric acid which is formed by the interaction of the free sulphuric acid and the added salt, and also probably to the presence of basic chromium chloride. This no doubt explains the use of salt in tanneries where a high quality chrome leather is produced.

The effect of neutral sulphates is rather different for here we have the sum of two opposing tendencies. On the other hand the swelling would increase with the decrease in acidity of the solution caused by the interaction of the sulphuric acid with the added sulphate, but the latter would again tend to exert a repressive effect. An increased swelling might therefore result from the addition of comparatively small quantities of sulphates which would be valuable not only in increasing the yield of chrome sole leather but might possibly help to obviate the loose flanks obtained in box calf manufacture. From Porter's results,[12] the repressive

[11] The Action of Neutral Salts upon Chrome Liquors, A. W. Thomas and M. E. Baldwin, *J. A. L. C. A.*, 1918, 248.

[12] The Swelling of Hide Powder, *J. S. L. T. C.*, 1921, 259; 1922, 83.

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action of the sulphate would seem to render this improbable, but the retardation of the tanning caused by the presence of the added sulphate will allow more time for the swelling action to come into play before the fibre is fixed.

The following preliminary experiment in this connection may perhaps be described. A chrome stock liquor was prepared by reducing sodium dichromate with SO_2 and the resulting solution boiled to expel the excess. This was then diluted so that the chrome content of the resulting fifty-four litres of liquor was 0.3 per cent Cr_2O_3, and divided into two equal portions A and G. From the equation

$$Na_2Cr_2O_7 + 3SO_2 + H_2O = 2Cr(OH)SO_4 + Na_2SO_4$$

it will be seen that the ratio of Cr_2O_3 to Na_2SO_4 is 152 to 142 or approximately 1 : 1. Five hundred and seventy grams of Glauber's salt was added to liquor G to increase this ratio to 1 : 4, thus making the solution contain 1.2 per cent of Na_2SO_4. A delimed and bated calfskin was cut down the back and each side divided into pieces which were numbered to correspond with the position from which they were taken. These were all evenly slicked out, weighed and the pieces comprising each side put into the liquors A and G respectively. After various time intervals the pieces were taken out, slicked, weighed and returned to the liquors until they stood the boiling test, covered with sacking to age in the wet state, dried and weighed.

The weights of the pieces are given in the following table, the letters G and A referring to the liquors with and without Glauber's salt respectively:

TABLE II.

Time (hours)	Series I						Series II					
	I_A	I_G	II_A	II_G	III_A	III_G	I_A	I_G	II_A	II_G	III_A	III_G
0	47.0	46.5	57.0	58.0	91.0	90.0	34.0	34.0	33.0	33.0	49.5	49.5
1	44.5	51.0	57.0	62.0	—	—	32.5	33.5	33.5	34.5	50.0	51.0
2	46.0	53.0	58.0	62.5	94.0	96.5	—	—	—	—	—	—
19	44.5	48.5	57.0	61.0	94.0	100.0	—	—	—	—	—	—
22	—	—	—	—	—	—	33.0	33.5	33.0	34.5	51.5	52.0
84	47.0	49.0	61.5	64.0	—	—	—	—	—	—	—	—
Dry weights	15.8	15.9	19.6	21.5	29.3	30.7	12.2	12.8		12.6	18.7	19.3

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The pelt had a fuller and plumper appearance in the liquors containing Glauber's salt, but the increase in the dry weights may be due to a simple weighting of the leather by this substance. In view of this and the difficulty of even slicking no final conclusion can be drawn from this preliminary experiment until the work has been continued on a larger scale under definite conditions with regard to quantity of pelt and volume and strength of the chrome liquor but it seems possible that the swelling power of an SO_2 liquor can be increased by adding a small proportion of sodium sulphate.

The effect of adding other neutral salts has so far not been investigated but seems to offer a very promising field of research. In this connection the influence of sodium acetate may perhaps be cited for it is of peculiar interest since a green chrome liquor turns violet on the addition of this salt. A. Recoura has investigated the properties of chromic acetate and gives some interesting facts concerning the equilibrium between the violet and green modifications.[18] The effect of adding this and salts of several other weak acids to chrome liquors is under investigation for it seems quite possible that such solutions may have excellent tanning properties, especially with regard to the softness of the leather.

The influence of organic substances on chrome liquors is one which is of very great importance to the tanner, not only as regards the properties of the leather, but also the speed of the tannage. Procter, in the first edition of his "Principles of Leather Manufacture" published in 1903, states that by the addition of sugar or glucose to a chrome alum liquor a much fuller and plumper leather is produced which dries perfectly soft without even staking or fat-liquoring. This effect can probably be produced by many cellulosic materials, carbohydrates, proteins, sulphonated oils, etc. For example, by adding flour to an ordinary commercial chrome liquor not only is a fuller and plumper leather produced but the speed of tannage is considerably accelerated. This filling action is of great value not only in connection with the loose flanks in box-calf leather but also in the manufacture of glove leather. It is produced by liquors manufactured from bichromate which contain excess of organic re-

[18] The Isomeric Forms of Chromic Acetate, *J. S. C. I.*, 1899, 760, 829, 911.

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ducing agents such as glucose, starch, flour or whey, or by the addition of these bodies to a one-bath liquor directly. It may be added that here we have a distinct difference between iron and chrome tannage for Stiasny has shown that the tanning action in the former case is completely prevented by a protective colloid such as egg albumen.

The production of a solution with certain specific tanning properties may be approached in another way. Instead of adding foreign bodies the acid may be chosen to produce these effects. In any chrome liquor we have hydrolysis which yields a basic chrome salt and free acid. Since the swelling, and consequently the firmness of the leather, is determined by the acidity and the neutral salt content of the liquor it should be possible by varying these to alter the properties of the leather in any way desired. Hence if we replace the sulphuric acid by an organic, or other weaker acid, we shall get a lower hydrogen ion concentration and consequently less swelling and therefore a softer leather. This should be fuller since a highly swollen pelt would be empty on drying out unless filled with some filling agent or fat-liquor. The properties of the glucose liquor which Professor Procter put forward in 1897 are in part due to the presence of hydroxy-organic acids. This is also of interest in connection with the process described by O. Röhm[14] for improving alum tannages. He claims that a leather which is unusually resistant to water is formed if the aluminium be used in the form of acetate or formate. The preparation of chrome liquors containing acids other than sulphuric is however complicated by the fact that many of them would be destroyed if used in conjunction with bichromate. It thus becomes a question of dissolving precipitated chromium hydroxide in these acids, or adding their sodium salts to an ordinary chrome liquor.

There are several other factors which influence the properties of our tanning liquor besides its intrinsic composition such as its age and temperature. The effect of temperature in tanning has so far received little attention but it seems probable that it may be utilized to advantage. It has been shown that the amount of alkali which can be added to a chrome liquor before precipitation begins is in all cases lessened by increase in temperature

[14] Eng. Pat. 110,750, *J. S. C. I.*, 1918, 217A.

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and therefore tanning might be accelerated by warming in the later stages. This effect can be further developed by carrying out the neutralization in warm liquors.

Having chosen the liquor which is the most suitable for the kind of leather desired there are several points of importance in carrying out the tannage. The rate at which the liquor can be strengthened is determined by the thickness of the hide and the amount of motion, but if the basicity be carefully adjusted to the quantity of pelt and volume of the liquor a fairly high chrome concentration can be used at the start without danger of drawn grain. The neutralization of the leather can either be carried out after the tannage by means of sodium bicarbonate or borax, or more economically by neutralizing the liquor. Even in the former case it will be found to be beneficial to reduce the basicity of the liquor in the later stages of tanning since this proceeds at the greatest speed when the liquor is almost, but not quite, at the precipitating point and produces a more saturated tannage. For this purpose the method of control proposed by Professor McCandlish[15] is the only one which can be regarded as satisfactory. The quantity of the neutralizing agent required to bring the liquor in the paddle or drum to this condition is readily calculated from the number of cc. of a standard solution which is required to produce a permanent turbidity in a portion of the liquor and there is little danger of carrying the neutralization too far.

The next point which arises is the completion of the tannage. The question as to what constitutes a properly tanned leather is important and is dependent on the kind of leather and the use for which it is intended. The boiling test is generally regarded as the criterion of complete tannage but it should always be carried out after neutralization. It has been shown[16] that the shrinkage obtained is dependent on the acidity, and the view has been put forward that the feel rather than the absence of shrinkage should be regarded as the essential feature of this test. There should be no horniness or curling at the edges, but the shrinkage is of secondary importance for it is more often a sign of acidity rather than a lack of chrome. In the experiments described on the

[15] The Analysis of One-Bath Chrome Liquors, *J. A. L. C. A.*, 1917, 440.

[16] Chrome Tanning I, *J. S. L. T. C.*, 1920, 215.

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influence of neutral salts on the progress of tannage, referred to above, it is interesting to note that more shrinkage was observed with liquors containing sodium chloride than with sodium sulphate.

In conclusion, one more problem which is of importance both to the theory and practice of chrome tanning may be mentioned. A very marked improvement in the quality of chrome leather is obtained by allowing it to lie in pile, or horsed up, overnight immediately it comes out of the tanning liquor. The way in which this changes the properties of the leather is rather obscure but possibly the basic chrome salt on the fibre may hydrolyse further. At any rate the chrome becomes fixed to a greater extent and it is generally stated that the acidity increases. Thus neutralization is very often carried out after this ageing in the wet state to prevent the considerable loss of chrome which would otherwise occur and to eliminate any danger of decomposing the fat-liquor with consequent deposition of greasy matter on the grain of the leather. On the other hand if the neutralization is effected in the liquor careful attention must be paid to the after-treatment.

The author wishes to express his indebtedness to Mr. Glover and the Directors of the C. W. S. for kind permission to present this paper.

REPORT OF COMMITTEE FOR THE DETERMINATION OF THE ASTRINGENCY AND PENETRATING VALUE OF TAN LIQUORS

R. O. Phillips, Chairman

Some time ago I suggested to the Secretary of our Association that we should have methods for the determination of astringency and for the determination of the penetrating value or rate of diffusion of tan liquors.

In going through the literature it was rather surprising to find that practically no attempt has been made to measure these two very important tannery factors by a definite standard method, which would report results of value to the tanner. The more service the chemist can render to the tanner, the better will be the position of the chemist in the leather industry. There are other values of tan liquors and extracts which the laboratory could de-

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termine and which would give considerable information to the tanner. These should be perhaps included on the official analysis form for tanning extract and liquors and some of them will be mentioned later in this paper.

To begin, as I suggested to the members of this committee some time ago, the work as originally outlined by the Council for this committee, should be divided into two parts, and it is my suggestion that two Committees have charge of the work. I propose, if in accordance with the ideas of our Council, that another committee be appointed in addition to this Committee to be known as the "Committee for the Determination of the Penetrating Value of Tan Liquors," and that the present committee be known as the "Committee for the Determination of the Astringency of Tan Liquors." The writer does not consider that astringency and penetration have, necessarily, any relation to each other.

While I was in Europe this past winter I made numerous inquiries as to any work done there along the lines of astringency or penetration, and found, as far as I was able to ascertain, that practically nothing has been accomplished there for the measurement of these two important tannery values. Nearly every leather chemist with whom I talked in England and Germany wondered that more work along these lines—that is to standardize a method which would report a figure of value to the tanner—had not been undertaken before.

In Germany I found that Dr. Moeller had some years ago attempted to measure astringency by the contraction of hide substance, but apparently without much success. Prof. Stiasny of the Institute for Leather Chemistry is at the present time carrying on an investigation of the comparative astringencies of some tanning materials but he did not tell me the method he is using. He has promised to send me the results of his work.

In commencing the work of this Committee it was necessary to first find a proper definition of the two values which we are to measure. A definition for penetrating power is simpler to define than one for astringency. From the eight members of this Committee I have received definitions from only three collaborators.

Penetration is the time rate of diffusion of tannin through hide. We are primarily not interested in the rate of diffusion of

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the non-tannins in this work except in so far as they may help or hinder the rate of diffusion of the tannin. It should not be extremely difficult to find a method which will measure this property of tannery liquors and give concordant results in different laboratories.

In regard to the use of gelatin jelly for the measurement of either astringency or penetration, all of the members of this committee from whom I heard agreed that gelatin jelly, being practically structureless, would probably not be best to use for these measurements. I am quite of the opinion that gelatin jelly should not be used unless, of course, we do find that it gives us values comparable with hide substance. I think that a great deal of the work which has been done using gelatin jelly may be of little value since it is an entirely different medium than hide substance.

Thomas[1] has shown by experiment that the rate of diffusion of tanning extracts into gelatin jelly is usually greater the greater the ratio of non-tannin to tannin in the extract. While this is perhaps usually true it is not in every case for much depends upon the type and character of the non-tannin. Wilson and Kern[2] state that the speed of penetration is greater the greater the concentration of non-tannin capable of combining with hide substance. There is, however, a slowing up or retarding action on the rate of penetration if non-tannins of certain types be present such as substances of high colloidal degree or non-tannins that may decrease the acidity, thereby lowering the difference in electrical potential between the hide and the tannin. The rate of penetration of tannin into gelatin jelly is a function of the hydrogen ion concentration and Wilson and Kern[2] have shown that the rate of diffusion varies with different pH values for different tanning materials. In regard to the theory of tanning I am inclined to accept Bennet's adsorption hypothesis[3] which explains the origin of the electric charge on the colloid particles as an adsorption of the electrically charged ions.

It has also been shown by Wilson and others that the astringency of a tan liquor is inversely proportional to the non-tannin content or is proportional to the purity. I believe also that astrin-

[1] *J. A. L. C. A.*, Vol. 15, (1920), pp. 593.
[2] *J. Ind. and Eng. Chem.*, Vol. 14, (1922) p. 45.
[3] *J. Soc. Lea. T. Chem.*, Dec. 1917, pp. 169.

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gency may be a function of the difference in electrical potential between the hide and the tannin. From this it is seen that probably both penetration and astringency rest on the ionization theory as well as to some extent on the non-tannin content of the tan liquor. A mellow tan liquor usually penetrates fast while as astringent one usually penetrates slow.

Concerning a definition for astringency, do we mean the time rate of combination of tannin with hide substance, or do we consider astringency as a contracting influence rather than in a leather forming sense. If we think of astringency as the time rate of combination of tannin with hide it may become confused with penetration. If we do measure the time rate of the formation of the hide-tannin compound it will be necessary to differentiate between the hide non-tannin combination and the hide-tannin compound, for as we know, the smaller non-tannin particles usually move into the hide substance faster than does the tannin and partly by protecting the hide substance reduces the astringency.

I would like to obtain the idea of the members of the Association as to exactly what they consider astringency to be and whether or not astringency can be generally defined as the contracting influence of the tannin on the hide. I think it essential that before proceeding with the formulation of a method that we settle definitely the definition for astringency, limiting its meaning to a point where it will not be confused with other factors.

Following are some of the methods suggested by the members of the Committee:

Mr. R. E. Porter suggested that it might be possible to measure astringency by using hide powder and shaking the tan liquor out for a certain time with an excess of tannin in order that only the most astringent tannins be taken up to the exclusion of the mellow tannins. The combined tannin might then be determined as in the official method by difference or by Kjeldahling as in the Wilson method, or the hide powder could be subjected to the plumping action of a weak standard acid solution showing that the powder which plumps the least has been subjected to the most astringent tannin.

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There are many good points in this method which so far as I known has not yet been tried. If the definition which we give to astringency is the time rate of combination of tannin with hide substance this method might work well, or would the mellow tannins on account of their rapid diffusion throw the method into error. There is much room for study and thought in connection with this method.

It has been suggested that the contraction of hide cannot be used for the measurement of astringency due to the fact that the plumping action of many liquors would interfere considerably in the measurement of such treated hide either by area, volume or weight. I think that most tanners and chemists when thinking of astringency consider it a contracting influence, although it has been pointed out to me that a tan liquor may be astringent and produce an astringent effect without appreciably contracting the hide or drawing the grain. If such a liquor is astringent the measurement of contraction would not be an indication of astringency. It all comes back to our definition of astringency and before the Committee goes on with this work I suggest that the Association state clearly what our conception of astringency is. The Chairman of this Committee is inclined to believe that astringency is a contracting influence and that it may be measured apart perhaps from the leather-forming properties of the tan liquor.

Mr. S. K. Johnson suggests that it will be very difficult to differentiate between astringency and penetration. He refers to the fact that a tannin which diffuses rapidly and does not unite rapidly is a mellow tannin, and a tannin which unites rapidly and does not diffuse is called an astringent one.

Mr. L. H. Englund suggests that it may be possible to measure astringency by means of surface tension which might give us relative values. This method might give us good results if the surface tension between the hide substance and the liquor could be measured, but to measure the surface tension between the tan liquor and air would not seem at first to be a function of astringency. We know that certain substances in small amounts can be added to a tan liquor to reduce its surface tension greatly which probably

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have no appreciable effect on the astringency. Before discussing the value of surface tension measurements, however, definite data must be obtained.

Mr. Hayes suggests that we consider astringency as a contracting influence and that if we accept this definition for astringency the extract which possesses the greatest astringency would permit the minimum swelling of hide powder and that this repression could be measured by the Claflin method for estimating the plumping value of liquors. This method may work very well, and it will be tried.

An electrometric method for determining astringency would probably not give results of value since various acids would lead us into error. This method, however, was suggested.

Leaving the subject of astringency and penetration, I think it would be of value to the tanners to appoint a Committee to determine the concentration of maximum and minimum solubility of the various types of tanning extracts. The various extracts have an aqueous solution concentration point of minimum solubility which varies with different extracts, and I believe it would be of value to determine where the point of greatest insolubility is for the different extracts. Another subject that I would like to mention is that the solubility of vegetable extracts as represented at analytical strength by the insolubles upon the analysis form does not indicate the true solubility of the extract in the tannery. I think it would be worth while for the Association to consider a solubility test apart from the insolubles given in the present analysis report.

Another subject which I think the Association should consider is a standard method for determining the weight giving properties of a tan liquor. At the present time one hears conflicting reports as to the weight-giving properties of various tannins. I think that a standard method to determine the weight-giving properties of the various tannins would give the tanner information which he now only obtains by experience, reading or hearsay. Considerable has been written of course on the weight-giving properties of the various vegetable tannins, but the order of weight-giving properties in some instances conflicts.

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A POSSIBLE THEORY OF CHROME TANNING *

By F. C. Thompson and W. R. Atkin

The Procter-Wilson theory of vegetable tanning has lately received further support by the researches of Loeb in America and by recent work carried out at Leeds in the Procter International Research Laboratory. Briefly stated, vegetable tanning is due to the neutralization of the positive electrical charge possessed by hide in the presence of acids, by the negative charge of the tannin particles, with consequent formation of a hide-tannin compound. Whilst this theory effects a logical co-ordination of the observed facts of the vegetable tanning process, chemists so far have not been able to apply similar considerations to chrome tanning. Wilson assumed that the tanning agent must be colloidal chromic hydroxide and that as this body is *positively* charged in acid solution, the combination with positively charged hide cannot be an ordinary colloidal precipitation such as is obtained by mixing positive and negative sols. Wilson then went on to formulate a chemical theory of chrome tanning involving the formation of chromium collagenates. This point of view has been extended by Thomas and his co-workers who speak of tetra- and octa-chrome collagens. These views have obtained considerable support but the writers are of the opinion that many chemists must, like themselves, feel somewhat uneasy when two theories of a totally distinct character are provided for two processes which show such close resemblance to each other as do the vegetable and one-bath chrome tanning processes. The writers are engaged in a survey of the purely chemical literature bearing on chromium sulphates and chlorides, normal and basic, and this survey, though it has extended to over eighty papers, is not yet complete. To add to the difficulties one finds numerous contradictions on points of importance, but one fact at least seems to be definitely established, *i. e.*, that at any temperature between 0° C. and 100° C. there is a definite equilibrium existing between the green and violet forms of chromium sulphate. Both are present, though at low temperatures there is very little green, and at high temperatures very little violet. Equilibrium is quickly

* Read at the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Ontario, Canada, June 23, 1922.

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reached in the change *violet* ⟶ *green* by raising the temperature but the reverse change *green* ⟶ *violet* on cooling is very slow in the case of sulphates, though more rapid with chlorides and still more so with nitrates. We have also to consider hydrolysis equilbria for both the green and the violet forms and these depend on temperature and dilution.

We here venture to put forward the view that chrome tanning is effected by a negatively charged anion or colloidal particle containing chromium and arising from the green form of chromium sulphate.

Quite recently, Pauli, one of the most eminent investigators of colloids, has proved that basic solutions of zirconium chloride and aluminium chloride contain both negatively and positively charged particles of zirconium or aluminium compounds and has even gone further to suggest that gold sols owe their stability and negative charge to the presence of a negatively charged complex anion containing gold. By this hypothesis, therefore, chrome tanning is caused by the neutralization of the positive charge of acidified pelt by the negative charge of the chrome complex. Thus chrome tannage would be explained in a similar way to vegetable tannage and other tannages by colloidal silicic acid and sulphur—both of which are negatively charged in solution.

It is most improbable that the actual chrome tanning agent is negatively charged chromic hydroxide though Powis has prepared colloidal ferric hydroxide possessing a negative charge. The usual colloidal ferric hydroxide prepared by dialyzing ferric chloride has a positive charge, but Powis succeeded by working in a slightly alkaline medium. The negative ferric hydroxide was precipitated by the addition of a small quantity of acid, and such would be the fate of negative chrome hydroxide if present in chrome liquors, which are always distinctly acid. The actual chrome tanning agent must be one that is stable in acid solution and also possesses a negative charge so that it would migrate to the anode (positive pole) if its solution were electrolyzed.

Actually we have been able to collect quite considerable evidence in support of the view that such a negatively charged chrome complex does exist in chromium sulphate solutions. (A) Several workers have prepared varieties of chromium sulphate which in solution do not yield precipitates with barium chloride,

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nor with ammonia nor sodium phosphate, thus showing the absence of chromium or sulphate ions. The tests were made in the cold as on boiling precipitates were yielded in all cases. Precipitates were also formed after the solutions were allowed to stand before being tested. We have found that a commercial chromium sulphate supplied in the form of dark green hygroscopic scales behaved in an exactly similar manner. These results show that the Cr and SO_4 exist in a complex form but give no indication as to the sign of the electrical charge of the complex.

(B) Bassett found that by electrolyzing a green solution (prepared by reducing chromic acid by sulphur dioxide in the cold), that a green boundary moved to the anode and a violet boundary to the kathode. The violet boundary represents $Cr^{\cdots}$ ions but the green anodic migration points to the presence of a negatively charged green chrome complex. He noticed similar behavior with a freshly boiled and cooled violet solution which would then contain a considerable amount of the green form.

Ricevuto electrolyzed chrome alum, and as this was rendered more basic by the addition of alkali, he noticed an increased anodic migration of a green substance which he thought was chromium hydroxide.

(C) Pauli, in the work alluded to above, has made electrometric determinations of $H^{\cdot}$ and Cl', along with measurements of conductivities, freezing points and transport numbers of solutions of basic salts of zirconium and aluminium. He comes to the conclusion that the occurrence of negative together with positive colloid complexes is a general phenomenon in metal oxide sols. He formulates a possible negative zirconium complex as follows:-

$$Zr(OH)_4 \,.\, Zr\,O\,Cl_2\ \overline{Cl}_2/\overset{+}{H}_2$$

of which the chromium analogue would be

$$Cr(OH)_3 \,.\, Cr\,O\,Cl\ \overline{Cl}/\overset{+}{H}$$

Such a substance would tan as do the vegetable tannins. If it exists in equilibrium with other chromium complexes then it would be produced as tanning proceeded even if originally present only in small amounts.

(D) Some interesting experiments have been carried out by the writers with benzidine base. This substance dissolved in

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amyl acetate and shaken with chromic *chloride* solutions gives an immediate and bulky green precipitate.

The "benzidinium" ions are of course positively charged and the precipitate will therefore be due to a negatively charged substance in the chrome liquor. In confirmation of this, copious precipitates are given by all vegetable tannin solutions with benzidine. In addition solutions of aluminium nitrate and ferric chloride yield precipitates with this reagent.

The writers are aware that much experimental work is needed before such a theory as the above can be accepted, and they intend to take up such work in the near future, confining themselves to the chemical investigation of chromic solutions. They feel however that to bring chrome and vegetable tanning theories into line will be a considerable achievement.

JOINT CONTRIBUTION FROM THE PROCTER RESEARCH LABORATORY AND THE LEATHER INDUSTRIES DEPT., UNIVERSITY OF LEEDS.

May 29, 1922.

BOOK NOTICE

NATURE AND CONTROL OF TANNERY PROCESSES. By Joseph R. Lorenz. Published by the *Shoe and Leather Reporter*, Boston. Price $2.00.

This treatise was published as a special issue of the *Shoe and Leather Reporter* and is devoted to the principles and practice in the manufacture of chrome-tanned upper-leather. The author describes the principles underlying certain of the operations simply and clearly so that it should be of particular value to the practical man and manufacturer.

The subject matter is divided into chapters on the soaking of hides, first fleshing, the liming process, deliming and bating, the pickling process, the chrome-tanning process, retanning of chrome leather, neutralizing of chrome-tanned leather, the fat-liquoring process, the coloring of leather and chrome-tanned white leather.

Besides a number of self evident typographical errors there are several statements made that are in error but these do not detract from the value and usefulness of the book.

ABSTRACTS

Directions for Tanning and Dressing of Furs. By JOSEPH DIXON, University of California, College of Agriculture, *Circ.* No. 237. Directions for home tanning of small fur skins are given. These directions are based on twelve years' experience of the author and skins tanned in this manner in 1909 for the California Museum of Vertebrate Zoology are still in good condition. R. W. F.

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The Animal Hide as an Amphoteric and Colloidal Protein. By M. A. RAKUSIN. *Kolloidchem. Beihefte,* 15, 103-184 (1922). That there is a close relation between dyeing and tanning was first pointed out by Knapp, and apparently rediscovered by Zacharius; however, Meunier and Seyewetz do not believe there is such a relation. (The author has not had access to foreign literature since 1914 and many articles before that time were accessible only through the Russian Journals).

Theory of the Dyeing of Animal Hide. (A) The composition of animal hide in its relation to coal tar dyes.—Knowledge of the chemical composition of the hide as well as of the dye is necessary in developing a theory of dyeing. Schroeder and Passler [*Dingl. polytechn. J.,* 287, 11, 12 and 13 (1893)], gave figures for the elementary composition of twelve important animals. They concluded that hide substance or gelatine respectively are chemical individuals or at least are very nearly so. Hide powder and gelatine give the same color reactions as the proteins; that is the Biuret and Ostromyslenski (red color with a grain of picraminic acid) reactions for nitrogen and the carbohydrate reactions of Molisch and Pettenkofer. The sulphur in hide is present in the cystin while in gelatine it is present as chondroitin-sulfuric acid, an acid which does not give any of the reactions of proteins but reacts with barium chloride and which is laevo-rotary and not dextro-rotary as previously stated.

(B) Action of acid or basic aniline dyes on animal hide.—The positive adsorption of the dye in the dyeing of hide is accompanied by a negative adsorption, *i. e.,* an adsorption of the solvent or a swelling. The acid dyes, eosin and congo red, and the basic dyes, bismark brown and crystall violet were irreversibly adsorbed by hide powder without a mordant from boiling water or 95 per cent alcohol; with the exception which can not be explained that the adsorption of crystall violet from alcohol was reversible. Methyl orange was also irreversibly adsorbed from water. The dyeing of animal hide is, therefore, beyond doubt a chemical process.

(C) Methylene blue.—Methylene blue, a basic dye, was washed out of hide by either boiling water or alcohol. However, since the source and purity of the dye were not known and since this result is contrary to practical experience the experiment must be repeated with pure dye.

(D) Methyl orange.—Although methyl orange is adsorbed by hide or gelatine, gives a good color and is light fast, it is reversibly adsorbed from water, although irreversibly adsorbed from alcohol. Freundlich found that a tendency to dissociate checked adsorption and Rakusin has data (not yet published) to prove that irreversible adsorption of electrolytes does not occur. Apparently therefore methyl orange is an electrolyte in water and a colloid in alcohol.

(E) The part played by the individual constituents of hide during dyeing.—Dyeing hide is a special case of dyeing proteins, which easily form irreversible compounds with acid or basic dyes. Strong alcohol removes carbohydrates, polypeptides and amino-acids from native pro-

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teins. After the protein is dyed, alcohol removes colored polypeptides and amino-acids and colorless carbohydrates. The carbohydrates can be quantitatively recovered after decolorizing the filtrate with charcoal.

(F) Experimental characteristics of the process of dyeing hide.—Zacharius has stated that hide substance can only take up colloidal dyes but this is not true. Hide substance unites irreversibly without mordanting (therefore chemically) with either acid or basic dyes, because it is amphoteric. Only the component of the hide which contains nitrogen is dyed. Dyes form more stable compounds with hide than tannin for the latter is reversibly adsorbed. Cotton only takes up basic dyes after mordanting either with tannic acid or with some substance which can unite with the dye and fix it to the fibers. On the other hand Grasser's "animalized" cotton (cotton treated with formaldehyde and gelatine) can be used for tanning experiments with tannin since tannin unites chemically with basic or amphoteric substances.

(G) Vegetable dyes.—Vegetable dyes such as litmus or turmeric were readily washed out of hide and therefore do not dye it, although they have been used occasionally in practice to color leather.

Theory of Tanning with Tannin. (A) The problem of the constitution of tannin.—The knowledge of the chemical nature of the aniline dyes and the conception of animal hide as an amphoteric colloidal protein mixed with an inert crystalline sugar, made possible an explanation of the dyeing process. The tannins are, however, not well known. It is certain that tannins from different countries have different structures. They are always accompanied by sugar and gallic acid and are very weak acids although they can be made to liberate CO_2 from carbonates.

(B) Characteristics of the action of tannin on hide and gelatine.—Tanning is considered by certain chemists (Stiasny) as a purely physical process while others (Fahrion, Meunier and Seyewitz) consider it purely chemical; while it is usually thought to be a complicated physico-chemical process. Payen first investigated the reversibility of tanning and found in three tests that, 6.469 per cent, 8.09 per cent and 7.3 per cent of tannin was washed out of leather by water. Schmidt found that either water or alcohol removed the tannin and set free albumin from "tannalbin" while other work has shown that the reaction between tannin and proteins is reversible. On treating an aqueous tannin solution with a quantity of gelatin equal to 3 per cent of the solution a decrease in concentration was found instead of an increase as with dyes. This is the only exception to the rule that we have negative adsorption with gelatine, and it is also unusual since positive adsorption is usually only shown by porous colloids. Tannin was positively adsorbed by kaolin and hide, the negative adsorption being negligible. The author concludes that the tanning of animal hide by tannin in water or alcohol is reversible even at ordinary temperatures and that the tannin compound is therefore less stable than the compound with aniline dyes especially the acid dyes. The surface tension or possibly the slight chemical relation between tannin and hide or gelatine exceeds the swelling force and this provides a means of calculating

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the mechanical equivalent of swelling and perhaps also the chemical relation of tannin to hide substance.

(C) The part played by each component of the hide during the tanning process:—

Color reactions of hide	Biuret	Molisch	Ostromyslenski
Before treatment with tannin	+	+	+
After treatment with tannin	—	+	+

Only compounds containing nitrogen, and giving the Biuret reaction react with tannin. Compounds containing the NH_2 group (Ostromyslenski reaction) do not unite with tannin but do unite with aniline dyes. The sugars do not react with tannin and in practical tanning they will therefore accumulate in the old liquors, adding to the sugars from the extract.

Cause of the astringency of tannins:—

NITROGEN REACTIONS OF ALBUMINS

	Biuret	Millon	Xantho-prot	Lieber-mann	Adam-kew	Ostromy-slenski
Before tanning with tannin	+	+	+	+	+	+
After tanning with tannin	—	+	—	—	—	—

Tannin binds all groups except the tyrosine (Millon's reaction) and this is the source of its adstringent or physiological action. Also tannin robs gelatine or hide of its ability to swell, since the relation of tannin to these amphoteric substances is greater than the force causing swelling.

The adsorbent character and the velocity of tanning.—From the above it is clear that the action of tannin on proteins and especially on hides is a reversible adsorption, accompanied by a chemical reaction between the weak acid, tannin, and the amphoteric proteins of the hide. With the exception of the work of Schroeder and Passler, which was done before the idea of negative adsorption was introduced, practically no work was done on adsorption until the present time. Rakusin treated 3 per cent of hide powder for one hour with tannin solutions of various concentrations and found that the Ostwald-Freundlich adsorption rule was followed. Since the basis of positive adsorption is surface tension, this factor must exceed that of the chemical relation between protein and tannin, which in turn was shown above to exceed the swelling factor. The influence of time and the method of adsorption will be investigated, and it has already been found that these factors have no influence on the adsorption of albumin by aluminum hydroxide. With hide powder the adsorption was complete in one hour and Freundlich's expression "every adsorption is practically ended in a few minutes" probably is true of tanning. However, the velocity of commercial tanning is much lower due to the reversibility to cold water and to difference in structure between hide in large pieces and as powder. The principal means that have been used to increase the velocity of tanning is by use of an electric current. Rover, in 1896, using a 100-volt direct current was able to force 7.377 kilos of tan liquor per hour through each square meter. The action was

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proportional to the potential but not to the current. Williams compared the action of direct and alternating currents and found that the direct current rapidly destroyed tannin but that the alternating current had little effect on tannin while it increased the tanning velocity.

Theory of Tanning with Formaldehyde and other Organic Substances. Formaldehyde.—The tanning action of formaldehyde was first observed by Trillat and its use in alkaline solution was patented by the English firm Pullman & Co., in 1898. Although a careful study has been made of the action of formaldehyde on gelatine, various proteins and amino acids, the chemistry of formaldehyde tanning rests only on hypothesis. Amino acids, which are inner salts, react with formaldehyde as follows: (R may be any radical as CH_2 in glycocoll).

$$\begin{array}{l} R-NH.H_2 \\ \diagdown \quad \diagdown \\ \quad CO-O \end{array} + HCHO = H_2O + \begin{array}{l} \diagup N = CH_2 \\ R \\ \diagdown COOH. \end{array}$$

Since acid is set free this reaction has been made the basis for a quantitative method for the determination of amino-acids in the absence of sulphides. Bach, Benedicenti and Schwarz found that albumin solutions could not be coagulated by heat after treatment with formaldehyde. Compounds of formaldehyde and casein have been patented for use as substitutes for horn, ivory, etc., while the compound with gelatine known as Glutol or Glutoform, has found a use in surgery as an antiseptic. Keratin or wool are more resistant after treatment with formaldehyde and wool so treated can be dyed with sulphur dyes which require an alkaline bath. Practically, formaldehyde is used to fix the swelling of the swollen hides so that they can be started in stronger liquors and also to produce a thicker, stronger and more durable leather. It is especially valuable for use with extracts. The action of formaldehyde on hide must be chemical and the same as the reaction with amino-acids. The following table shows that in the presence of formaldehyde proteins, ferments, etc., are not able to give any of the nitrogen reactions except the Ostromyslenski.

Whether the formaldehyde acts as such or rather the aldehyde group —CHO is difficult to state for an investigation must be made of the filtrate after it has been freed from components of the hide which contain nitrogen; also, in addition to aldol-like compounds, formaldehyde and carbohydrates give compounds which represent ether-like derivatives of methylene and these might give the reactions of Molisch and Pettenkofer.

Tanning with aldoses.—No nitrogen reactions were obtained with albumin, gelatine or hide powder after treatment with arabinose or dextrose. This is of practical importance since aldehydes are formed in the two-bath chrome process when the reducing agent is alcohol or other organic compounds.

Tanning with Phenols.—(A) The sixteen substances used with formaldehyde were also treated with pure phenol and, as was the case with

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COLOR REACTIONS OF PROTEINS

		Nitrogen reactions						Carbohydrate reactions	
		Biuret	Millon	Xanthoprot	Liebermann	Adamkewitsch	Ostromyslenski	Molisch	Pettenkofer
1.	Egg albumin	—	—	—	—	—	+	+	+
2.	Fibrinpeptone	—	—	—	—	—	+	+	+
3.	Casein	—	—	—	—	—	+	+	+
4.	Legumin	—	—	—	—	—	+	+	+
5.	Keratin	—	—	—	—	—	+	+	+
6.	Elastin	—	—	—	—	—	—	+	—
7.	Chondrin	—	—	—	—	—	+	+	—
8.	Gelatine	—	—	—	—	—	+	+	—
9.	Hide powder	—	—	—	—	—	+	+	—
10.	Nucleic acid	—	—	—	—	—	+	+	—
11.	Glycocoll	—	—	—	—	—	+	—	—
12.	Pepsin	—	—	—	—	—	—	+	—
13.	Papain	—	—	—	—	—	—	+	—
14.	Pancreatine	—	—	—	—	—	+	+	—
15.	Diastase	—	—	—	—	—	+	+	—
16.	Yeast	—	—	—	—	—	+	+	—

formaldehyde, none of the nitrogen reactions except the Ostromyslenski were given by the treated substances.

(B) The dihydric phenols, hydroquinone and pyrocatechin were used to treat the following substances: Albumin, pepsin-fibrin-peptone, casein, legumin, α and β glue, hide powder, nucleic acid, pepsin, diastase and pancreatine. The nitrogen reactions were again negative as with phenol.

(C) Meunier and Seyewetz patented the use of pyrogallol in 1914 and Rakusin has now investigated the action of the other trihydric phenols, phloroglucinol and oxyhydroquinone with albumin, gelatine, and hide powder. Again the same results were obtained for the nitrogen reactions. There is also a physiological action since pyrogallol colors hair or hide a brownish red and has been used with silver nitrate to dye hair. The ability of pyrogallol to absorb oxygen should also be kept in mind especially since there are those who still adhere to Fahrion's oxidation theory.

(D) Homologues.—Gelatine in the presence of the three isomeric cresols and thymol gave the usual results. Albumin in the presence of the cresols however, gave the Millon reaction and the cresols, therefore, do not unite with tyrosin. Thymol-treated albumin gave only a trace of Millon's reaction. Thymol and m-cresol, the only liquid cresol, tan hide while the o- and p-cresols do not tan, for hide treated with the latter two still gave the Biuret reaction.

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(E) Picric acid was used to treat the sixteen proteins and their derivatives and the color reactions were found to be the same as for cresols; that is picric acid united with all except the tyrosin group (Millon) and the amino bodies of unknown constitution which react with picramic acid (Ostromyslenski). Picric acid tans since the treated hide did not give the Biuret reaction. Picric acid also colors animal fibers (muscles, etc.), but does not color vegetable fibers.

(F) The action of α- and β-naphthol on albumin, gelatine and hide powder was investigated. α-naphthol bound all of the nitrogen groups of the proteins, so that all the reactions even the Ostromyslenski, were negative. β-naphthol on the other hand united with none of these groups for all the reactions were positive. Only α-naphthol therefore has possibilities of being of practical value although the β is given in the literature as a tanning material.

(G) Quinone. Meunier and Seyewetz found that leather tanned with 1 per cent of its weight of quinone was more resistant to water, acids or alkalies than any other kind of leather even chrome tanned. Quinone treated albumin, gelatine and hide powder gave only the Ostromyslenski reaction (Molisch's reaction was of course positive). Quinone probably will be of value for tanning without other materials as well as for combination tanning or for accelerating vegetable or chrome tanning.

(H) Ketones. Acetone-treated albumin, gelatine and hide powder gave the Biuret and Ostromyslenski reactions. Acetone, therefore, does not unite with the most important components, the Biuret group.

(J) Neradol, according to Austrian patent No. 58,405, is prepared by heating phenol derivatives, cresylic acid, crude cresol, etc., at 100-120° for several hours with the equivalent amount of sulphuric acid. Then, while cooling, one mol. of formaldehyde to each two mols. of phenol is stirred into the mixture, and finally the free acid is neutralized. Commercial Neradol is a pasty material, completely soluble in water, forming a weakly colored solution, and which after dialysis does not crystallize. On account of this last fact Stiasny designated it as a "semi-colloid" although he also considered it to be a synthetic vegetable tannin. Neradol reacts slightly acid and gives precipitates with solutions of gelatine, lead salts and aniline hydrochloride. The references (up to 1914) do not agree on the practical uses of Neradol but it seems it should prove of value since it contains the two tanning materials, phenol and formaldehyde. The determination of sulfuric acid in Neradol is important and a method for this has been worked out by Pässler.

(K) The various proteins after treatment with tannin failed to give only the Biuret, Xanthroproteic and Liebermann's reactions while the other organic materials prevented, as has been shown above, all reactions except the Ostromyslenski. Tannin has, therefore, weaker tanning properties than these other materials. This tanning property is also weaker since the reaction between tannin and hide is reversible at ordinary temperatures and this explains why practical tanning is so slow.

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Theory of Mineral Tanning.—The use of alum or iron alum for tanning is very old and chrome alum has found much use the last three decades. Armstrong found that manganese alum was too unstable to have any practical tanning value but that cerium might prove of value. He also produced leather resistant to acid or alkali by treatment with melted copper soap. Halogens may have a practical as well as a theoretical value while the action of sulphur may be similar to vulcanization of rubber. Inorganic tannins are substances which are adsorbed or which hydrolyse in water.

Tanning with Ordinary Alum.—Knapp found that animal hide took up 8.5 per cent alum and considered the tanning agent to be nascent aluminum chloride formed by reaction between the salt and alum. However, when he used three mols. of salt to one mol. of alum this reaction did not take place and yet the salt aided penetration or dialysis and acted as a dehydrating agent similar to alcohol. The action of aqueous solutions of alum on hide powder was found by Rakusin to be similar to a positive irreversible adsorption. There was not an adsorption of alum molecules, but a chemical reaction between the hide and the products of hydrolysis of the alum. Whether the hide substance unites with a basic product, or the NH_2 group unites with an acid product of hydrolysis is not known. Alum tanned hide gives the same protein reactions as untanned hide. Alum tanning seems to be closely related to the precipitation reactions of proteins.

The Tanning Action of Other Aluminum Salts.—Aluminum chloride is irreversibily adsorbed by hide powder and also by aluminum hydroxide; the leather gives the same nitrogen and carbohydrate reactions as alum tanned leather. Salt is always used and Melnikow thinks that the salt reacts to form the stable double salt, $Na\,Al\,Cl_4$. However, this double salt does not exist in solution and also no sodium chloride is found in the leather. A water proof leather can be made by impregnating leather with aluminum soaps. The tanning action of aluminum acetate was investigated since this salt can not liberate the destructive acids, hydrochloric or sulfuric. Many chemists even consider organic acids, except formic, harmful. Under conditions which would obtain in practice the acetate was not positively adsorbed and it can therefore have no true tanning action.

Tanning Experiments with Iron Salts.—Stiasny [*Koll. Zeitschr.*, **2**, 257 (1908)] has correctly stated that not only salts of metals of the third group but any salt which hydrolyses has a tanning action. Iron alum was found to be positively and irreversibly adsorbed by hide powder, gelatine and aluminum hydroxide and it is therefore a true tannin. Ferric chloride gave a yellow precipitate with hide powder or aluminum hydroxide although there was apparently a negative adsorption due to the method of analysis. Hide powder gave the same protein reactions after treatment with ferric chloride or sulphate as before treatment. Although ferrous salts do not tan, Mohr's salt was irreversibly adsorbed by aluminum hydroxide.

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Tanning Experiments with Chrome Salts.—Tanning with mineral salts, including chrome salts, was patented by Knapp in 1861, but chrome tanning was for a long time unsuccessful. It was the basis of "chromophotography" and carbon printing; the photographers holding that the gelatine was tanned by the chrome salt. Hide and gelatine are quite similar with the exception that the former contains cystin, a sulphur compound and therefore the tanning should also be similar; however, there is no general agreement on the chemistry of chrome tanning. On treating hide powder with a violet chrome alum solution the percentage adsorbed from higher concentrations of the alum approached zero, but in lower concentrations the adsorption was not 100 per cent as it should have been to follow Freundlich's rule. The process is therefore a chemical one in which adsorption plays a minor part and only after hydrolysis. The amount of chrome absorbed from all concentrations was very small; much less than with ordinary alum. Light chrome tanned leather, calf kid, contains 1.4 per cent while Austrian sole leather contains 7.77 per cent Cr_2O_3.

Vegetable tanned leather contains up to 50 per cent and averages 30-34 per cent vegetable material but this is easily washed out by water, while chrome is only washed out with great difficulty. The character of the combination between the hide substance and chrome is therefore the important factor; not the amount of chrome taken up. There was an irreversible adsorption of violet chrome alum by hide powder or aluminum hydroxide and of green chrome alum by hide powder. The albumin reactions of hide powder were not changed by treatment with chrome salts, including chromic chloride. Lumiere Bros. and Seyewetz (*Photogr. Wochenbl.*, 38, 300 (1903)) investigated the tanning action of many inorganic chrome salts, and found that all the salts of organic acids could be given a basic character. Chromates in the presence of strong acids or chromic acid reacts with gelatine or hide substance, liberating formic acid which unites with chromium oxide to form chromic formate and this salt tans the remaining gelatine or hide. The formic acid can be detected by distilling and testing with silver nitrate or by the smell.

The Rôle of Salt in Alum or Chrome Tanning.—Unhydrolysed salts, such as sodium chloride are not adsorbed by gelatine or hide but the solvent, water is adsorbed; that is there is a negative adsorption. Grasser (Untersuchung des chromleders und der chromgerbebrühen) investigated various chrome tanned leathers and found salt present (4.65 per cent) only in those tanned by the one-bath process. In two experiments with ordinary and with violet chrome alum in the presence of salt (three parts alum to one of salt) not a trace of salt was taken up and it therefore has no active part in alum or chrome tanning. Alum tanning is however usually considered impossible without salt and Procter holds the view that salt aids in the absorption of chromic acid by hide from undecomposed bichromate and also that salt reduces swelling in acid solutions since an equilibrium tends to be established between the chloride ions from acid in solution and those from the acid adsorbed by the hide, the latter

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acid being much less ionized than the former. Eitner found that less chrome and relatively more acid was adsorbed in the presence of salt, the effect being greater in acid or alkaline than in neutral solutions. Salt therefore seems to be unnecessary in chrome tanning.

The Rôle of Water in Different Methods of Tanning.—Tannin in alcoholic solution does not tan and the explanation given by Powarnin is that tannin may occur in two tautomeric forms; an enol form present in alcohol, which does not tan and a keto form which does tan and which is present in water. Water is necessary in chrome or mineral tanning to hydrolyze the salts. Chromic chloride in alcohol is not hydrolyzed and so has no tanning action.

The Rôle of Acids in Different Methods of Tanning.—Tanning is always carried out in acid solution but the acid must be carefully washed out after tanning. Only tanning with formaldehyde is carried out in alkaline solution, but here acid is formed by the action of the formaldehyde on the hide so the function of the alkali is probably to neutralize this acid.

Disinfection and Preservation of Animal Hides.—Disinfection with formaldehyde is carried out in the same manner as tanning except that the time of treatment is shorter. *Bacillus anthracis* is killed by formalin in a concentration of 1 : 500000 and the spores by 1 : 5000. Antidotes for formaldehyde depend on its reaction with proteins, which are derivatives of ammonia, to form protaldehyde ammonias. All metals which are irreversibly adsorbed must be poisonous. Mercuric chloride was found to be positively and irreversibly adsorbed by gelatine, forming a white precipitate. Mercurous nitrate and gelatine gave a black precipitate. There is, therefore, a precipitation and not an adsorption, and mercurous or mercuric protammonium compounds are formed, not mercury albuminates. Acid is set free and this causes the burning which accompanies mercury poisoning and is also the cause of the decrease in basicity of the blood. I. D. C.

Tannin Analysis II. By V. KUBELKA and F. BERKA. *Coll.*, **624**, 85-95 and **625**, 143-55 (1922). [See This JOUR., **16**, 388 (1921)]. Theoretically the filter method should give more nearly correct results than the shake method, but has not given concordant results since different laboratories do not use the same size of filter, time of filtration, etc., while every step in the shake method has been carefully standardized. The corrections, when using the filter method with unchromed hide powder are large, but with chromed powder are quite constant and the solubility of the hide powder is even less than by the shake method. A number of extracts were analyzed by the following methods: (1) The official, I. A. L. T. C., shake method, using freshly chromed hide powder, (2) Shake method with double detannization, (3) Shake method with ready (weakly) chromed hide powder, (4-9) Filter methods, using 7.5, 10 and 12.5-gram portions each of unchromed and of chromed hide powder.

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Extract	Per cent difference between methods 1 and 2 based Method 1	Method 3 gives + higher / − lower % results than Method 1	Difference between Methods 7 and 3 %	% Tannin by Method 1
Solid chestnut ext.	4.7	+0.7	2.3	64 0
Liquid chestnut ext.	5.4	+0.2	1.5	39.0
Liquid mimosa ext.	1.9	−0.3	1.7	31.0
Solid quebracho ext.	3.6	+0.5	2.3	71.5
Myrobolans without kernel	3.2	−0.8	4.5	48.9
Divi-divi	4.1	+0.2	2.3	43.4
Gambier	20.0	−0.6	12.8	46.9
Malleto bark	10.6	−0.3	5.5	39.3
Solid mangrove ext.	10.5	+4.3	2.8	59.8
Bohemian pine bark	12.8	+2.4	0.0	11.32
Liquid pine bark ext.	26.1	+2.9	3.7	17.6
Solid pine bark ext.	29.0— —25.1	+6.8— +5.3	9.1— —6.3	38.2— —37.9
Sulphite cellulose "Hansa"	24.1	+3.8	−1.6	17.4
Oak wood	6.0— —10.0	0.0	0.3	5.24 — 4.12
Liquid oak wood ext.	6 8	0.0	1.7	30.6
Syrupy oak wood ext.	7.0	+0.7	1.6	38.5
Solid oak wood ext.	20.0	+2.4	9.7	55.99
Pasty oak wood ext.	7.1	+2.2	3.0	39.78
Oak bark	11.6	+0.4	1.0	9.88
Solid oak bark ext.	26.0	+7.6	3.7	36.1

The results in column 2 show that the official method does not remove all the material that can be removed by hide powder. The differences are great enough in some cases to afford a means of distinguishing between certain extracts. The results in column 3 show that dry chromed hide powder is a better adsorbent than freshly chromed, and since dry chromed powder is used in the filter method this is one of the causes for higher results by this method. Unchromed hide powder was found to be unsatisfactory since it adsorbed less material than the chromed and also because more of it dissolves, especially in warm climates. By the filter method, 12.5 grams of hide powder was sufficient in all cases and 10 grams in practically all cases.

The official method does not remove all of the tannin due to the fact that an equilibrium is established between adsorbed and dissolved tannin. If this equilibrium can not be established, as in the filter method, more tannin is adsorbed as is shown in column 4. (In both methods, 7 and 3, 7.5 grams of dry chromed hide powder was used). In any quantitive method depending on a reversible reaction, the conditions must be arranged so that the reaction goes to completion in the desired direction. For example in precipitating zinc sulphide from a zinc sulphate solution, the concentration, temperature, etc., are not exactly specified but an acetate is added. Also the adsorption of non-tannin by hide powder can not be prevented. Future revisions of the method for tannin determination, which are necessary, must therefore be based on the filter principle.

I. D. C.

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The Influence of Heat in the Leather Industry. By J. KREMAR. *Gerber*, **48**, 111-3 (1922). That heat has a great influence on fermentation is generally known; for example liming is easier in warm weather since bacterial action then increases. Even if the daily variation in temperature of the various liquors is small the yearly variation is great and this makes it difficult to obtain a standard product. While many plants use older and stronger limes in winter it is best to heat the lime or soak liquors in winter so that the temperature is always within 2-3° of 70° F. The temperature of tan liquors can be regulated by using a liquor containing little sugar in summer and much in winter. In liming the loosening of the hair is the work of bacteria and their products; the malphigian layer and the hair roots being attacked before the corium. A great variety of bacteria develops, and much hide substance would be saved if the kind of bacteria and their action could be controlled. In this control temperature would be the most important factor. In acid swelling the acid unites with the hide liberating heat. Therefore, by Van't Hoff's law, an increase in temperature will decrease swelling and vice versa; thus if hides are to be swollen the temperature must be kept low. The temperature will of course influence other factors so that, for example, skins for sole leather are unhaired in limes at a higher temperature and then swollen in limes at a lower temperature. The temperature of the tan liquor influences its fermentation and acidity; a high temperature accelerates penetration but may destroy tannin. An increased temperature is advantageous in oiling or stuffing leather. In no other operation is temperature so important as in the drying of leather; ventilation however is of even greater importance. To save fuel drying chambers are designed so that as little heat as possible is used, and so that the air leaving the chamber is saturated with moisture.

The optimum temperature for the extraction of tanning materials varies with the material. The rule that the higher the temperature the better the extraction is not true since at a high temperature important components may separate out, thus lowering the tannin and increasing the non-tannin. The best temperature for the extraction of quebracho and mangrove bark is 80-90° C.; trillo and sumach, 50-60° C.; mimosa, 70° C., and myrobalans, 100° C. I. D. C.

A Simple Apparatus for Extracting the Solubles in Leather and Some Notes on Leather Analysis. By A. T. HOUGH. *Le Cuir*, **11**, 336 (1922). The present method of determining insoluble ash,—by taking the difference between total ash and the ash of the water solubles—, may lead to considerable error in the degree of tannage. Since the mineral matter is usually present as sulphate or sulphite, it is more accurate to treat the ash with sulphuric acid, re-ignite and weigh. The use of ammonium carbonate to break up bisulphates, is not recommended since it makes little difference in the results and may lead to loss by spattering. The author determines soluble mineral matter by ashing part of the water soluble matter and treating it with sulphuric acid. Insoluble ash is de-

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termined by ashing part of the water extracted leather as recommended by Riethof and Gayley [This JOURNAL, 13, 7 (1918)].

For the determination of water soluble matter, the leather is held in a glass cylinder, closed at each end with perforated filtering plates or in a gooch crucible covered by a plate which is held on by a rubber band. The cylinder or crucible, containing 5 grams of leather, is suspended near the bottom of a cylinder containing 250 cc. of water at 15-25° C. The crucible is raised 3-4 cm., twice, at half hour intervals; then brought near the top and left there over night. The extraction is quite complete. This apparatus was used for extracting grease from leather and gave results close to those obtained by the soxhlet method in spite of the fact that the solvent was cold in this and hot in the soxhlet method. I. D. C.

The Conditions for One-Bath Chrome Tanning. *Industries du Cuir*, **7**, 197 (July 16, 1922). Although much scientific work has been done, chrome tanning is little different to-day from what it was when first introduced. The objects to be accomplished in practice are economy in manufacture and quality of product. Either of two methods may be used in preparing the tanning solution. By one method chrome alum is dissolved in water and made basic with sodium carbonate. If the alum is dissolved in cold water a violet solution is obtained which tans hide slowly without swelling, while if dissolved in hot water a green, strongly acid solution is obtained which has very little tanning action but causes excessive swelling of the hide. In the latter solution the alum is largely dissociated into chromic oxide and free sulphuric acid. Although the neutralization with sodium carbonate tends to make the two solutions the same it is always better to prepare the tan liquor cold. The basicity is expressed as parts of basic chrome oxide per one hundred parts of total chrome oxide and solutions of basicity of 25-35 are commonly employed. The tanning solution may be more cheaply prepared by using sodium bichromate and reducing it with sulphuric acid and an organic material such as glycerine, glucose or starch. Since considerable heat is developed by the reduction the green salt will be formed and therefore it will be best to age the solution before use.

In tanning there is introduced into the drum, in the following order, (1) water, (2) salt, (3) the hide either pickled or not, (4) tanning liquor. Therefore the factors to be investigated are (1) how much water to introduce at first (influence of concentration on tannage), (2) influence of salt, (3) should the skin be pickled or not, (4) what quantity of chromic oxide should be used and what should be the basicity. Only the effect of concentration has been investigated so far. Experiments were made with calf-skins varying the time of tanning and the basicity and concentration of the liquor. It was found that the fixation of chromic acid was independent of the fixation of the sulphuric acid, relatively more acid being fixed at first. In non-basic solutions relatively large amounts of acid and little of chromic oxide were fixed. In basic solutions the quantity of acid fixed may or may not be greater than the chrome

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but the fixation of chromic oxide and acid seem to go hand in hand indicating the existence of basic chrome salts. Practically, the time of tanning should not exceed twenty-four hours and therefore a concentrated liquor must be used. There do not seem to be any bad effects by using concentrated solutions or by using less liquor than is required to bathe the hides. After tanning the skins should be allowed to stand for a while before rinsing since the amount of chrome washed out decreases with the time of standing and is practically zero in four days. I. D. C.

PATENTS

Making Extracts. Brit. Pat. 178,138. W. A. Fraymouth, London, J. A. Reavell, Kent, and Kestner Evaporator & Engineering Co., Ltd., London, Oct. 5, 1920, No. 28,174.

Making Extracts. Brit. Pat. 178,139. W. A. Fraymouth, London, J. A. Reavell, Kent, and Kestner Evaporator & Engineering Co., Ltd., London. Oct. 5, 1920, No. 28,175.

In the preparation of tanning-extracts, the usual leach pits are combined with a vat or vats which may be of the kind described in Specification 178,138 comprising an agitation zone and one or more quiescent zones. The powdered and fine particles of the crushed or milled tanstuffs are introduced into an agitation zone and are wetted by liquor pumped from the leach pits and then agitated by gas uplift tubes. The further introduction of liquor from the leach pits causes the liquor in the agitated zone to pass into a quiescent zone and to flow from the top thereof as a clear strong liquor.

Leather-Measuring Machines. Brit. Pat. 177,151. Krupp Akt.-Ges., Essen, Germany. Feb. 21, 1922, No. 5,034. Relates to machines of the type in which the lengths of a series of strips are measured.

Chlorination of Cellulose Lyes. Brit. Pat. 178,104. A. Schmidt, Paris. March 31, 1922. Sulphite cellulose lyes, after separation of sugar and concentration, are chlorinated by passing a current of chlorine through, filtering, and treating with a chlorate and hydrochloric acid. Soluble reddish-yellow products of acid character are obtained which are useful as tanning materials and as resin substitutes.

Treating Hides. Brit. Pat. 179,135. H. Renner and W. Moeller, Hamburg, Germany. Sept. 28, 1921, No. 25,705. In the manufacture of bates for leather from dung or materials containing enzymes, an activator such as magnesium or calcium hydroxide is added, the bate being extracted with a dilute solution of one of these substances and subsequently neutralized. Treatment of dogs' dung or the pancreatic gland in this way results in the increased formation and transformation of the pro-enzyme in consequence of the presence of hydroxyl ions, the concentration of which should be kept within certain limits. After extraction, the hydroxyl ions may be neutralized, preferably with lactic acid, so that the alkalinity does not exceed 0.1 per cent. Magnesium hydroxide is preferably used,

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as, owing to its low solubility, it may be added in the form of a suspension without exceeding the hydroxyl ion concentration.

Leather-Finishing Machines. Brit. Pat. 179,368. G. L. WILKS, Surrey. March 5, 1921, No. 7,207.

Treating Leather. Brit. Pat. 179,969. A. MCLENNAN, Ross, Herefordshire. Nov. 19, 1920, No. 32,680. Relates to processes for impregnating leather with india-rubber. According to the invention, the leather is treated with a clarifying or grease-removing solution prepared from a stock solution of crystalline powdered sulphur in carbon bisulphide or tetrachlorethane by precipitating the undissolved sulphur by the addition of acetone, ether and benzol and adding paraffin or petrol to the mixture thus formed. The rubber solution or solutions are formed by dissolving rubber in coal-tar solvent naphtha or benzol, thinned to the desired consistency by adding heavy grade petroleum spirit and paraffin or paraffin alone. The leather is sprayed with the clarifying solution, and when saturated is left for about twenty-four hours in a closed receptacle, being afterwards removed and allowed to dry. It is then buffed upon the flesh side and placed in a steam or hot-water jacketed receptacle containing the rubber solution. After one or more immersions, the leather is drummed in one or more further rubber solutions of increasing density. During the final drumming process there are added at intervals solutions containing gutta-percha, balata, gum mastic and gum dammar, and finally, chloride of sulphur solution. The chloride of sulphur may be mixed with the original stock sulphur solution or the two solutions may be placed successively in the drum.

Synthetic Tanning-Agents. Brit. Pat. 180,353. M. MELAMID, Frieburg, Baden, Germany. Nov. 26, 1920, No. 33,436. Synthetic tanning-agents are prepared by treating cresols, or the phenols derived from anthracene oil, or napthalene, with acetylene in the presence of mercury compounds and sulphuric acid; if the sulphuric acid is not present in sufficient amounts to give the sulphonated products direct the products are subjected to further sulphonation; or sulphonated cresols, sulphonic acids of the phenols derived from anthracene oil, sulphonated naphthalene, or naphthalene—α-or-β—sulphonic acid, are treated with acetylene in the presence of mercury compounds only.

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The American Leather Chemists Association

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The election and induction into office of a president of an association is usually an interesting occurrence. There are the exchanges of felicitations, regrets at being "off with the old," hopes and fears associated with the "on with the new." To some, the occurrence may be of only passing interest; to some it may be tinged with doubts; to some it may be a reason for rejoicing.

The Tanners' Council recently elected a president and with due ceremony he has assumed office. Because of the man, the event is of more than passing interest for our Association; is a real reason for rejoicing and is deserving of being chronicled in our annals.

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Fraser M. Moffat, the new President, is a tanner by right of birth, has a two century ancestry of leather forbears. His father made what was considered the best harness leather coming out of New York, and he himself was reared in his father's tannery. He ought, therefore, to be a practical, hard-headed, narrow-minded, non-progressive tanner. Strangely enough, he is not, but instead is a man of vision, appreciatively interested in the latest scientific developments bearing on an understanding of leather making. He has been Chairman of the Research Laboratory Committee of the Tanners' Council for the past several years, and it is through his faith in the value of scientific study, his ability to inspire others with the same faith, that the large measure of success achieved has been made possible.

This is not by way of saying that the practical side is lacking from his makeup, for no sooner were results in sight from the Research Laboratory that seemed to bear practically on the problems of the industry, than he started putting the information to use. The Research Laboratory developed certain facts as to the best method of curing hides for tannery use, and through the activities of Fraser Moffat a real interest in this subject was aroused among the packers, and we may expect definite improvement in the curing of hides in the not too distant future.

It cannot but mean much to our Association that a man so keenly in sympathy with the particular aspect of the making of leather to which our activities are devoted is at the head of the Tanners' Council. We should congratulate both the Tanners' Council and ourselves for the promise which the Presidency of Fraser Moffat holds for a fullness of understanding and a heartiness of co-operation between our Associations that must make for achievement.

F. H. S.

ELECTIONS

ACTIVE

Harbaugh, W. LeC., Elkton, Va.

ASSOCIATE

Cartwright, C., Railway Leather Works, Rochdale, England.
Longbottom, H. L., 5 Broome Street, Cotteslae Beach, West Australia.
Ludwig, K., Perkins-Campbell Co., 622 Broadway, Cincinnati, Ohio.
Martin, Giles, American Shoe Machinery Co., 299 Marginal Street, East Boston, Mass.

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CHANGES OF ADDRESS

Ellsworth, Paul R., National Aniline and Chem. Co., P. O. Box 718, Chicago, Ill.
Enna, F. G. A., Caixa Postal 344, Curityba, Estado do Parana, Brazil.
Greaves, T. G., R. F. D. 4, Charlottesville, Virginia.
Hart, Ralph, 656 West 162nd Street, New York, N. Y.
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B. D. WESTENFELDER
1865—1922

With the passing of Dr. B. D. Westenfelder, another of those affectionately referred to as the "Old Guard" has completed his contributions to the science of leather chemistry.

The number of those who, with a courage which now-a-days is not demanded of the rising generation, tackled the problem of putting the leather industry upon a scientific basis some thirty years ago, has during the past few years become increasingly small; and naturally induces in the minds of those who remain visions of the early struggles to gain a footing in the confidence of tanners.

Dr. Westenfelder in a marked degree was one of the faithful half dozen who originated and inspired this confidence, and therefore is worthy of wide-spread gratitude on the part of chemist and tanner alike. If memory serves us right, he was the first or second chemist to become identified with the actual manufacture

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of leather in the United States, and in the earlier years of leather chemistry his contributions to enlightenment were numerous and valuable.

A regular attendant at the meetings in Washington when a gathering of five or six chemists was considered a good meeting, his counsel was worth listening to as that of an earnest student of the many problems then only beginning to be recognized.

Of a retiring and gentle nature, in recent years he sought no prominent place in the affairs of the Association, which has grown from such small beginnings; but that his name and memory will always be held in esteem and honor for work well done, especially by those who knew him, will not be gainsaid.

ADOPTION OF PROVISIONAL METHODS

The following method for the Determination of Epsom Salts in Vegetable Tanned Leathers has been adopted by the Association as a provisional method.

Determination of Epsom Salts in Vegetable Tanned Leathers

Ash 5 or 10 grams of leather; carefully moisten ash with H_2O; add 15 cc. concentrated HCl; wash into a breaker; dilute to 50-75 cc.; add 2-3 drops of concentrated HNO_3; gently boil for a few minutes or heat on a steam bath for 15 minutes. Without filtering off insoluble matter add NH_4OH (approximately 1 to 1) slowly with constant stirring until nearly neutral but still slightly acid, then add dilute NH_4OH (about 3 or 4 to 1) and precipitate with a very slight excess of it. (If the NH_4OH precipitate does not have the characteristic reddish brown color of ferric hydroxide and there is known to be sufficient NH_4Cl present to hold in solution all magnesium, redissolve in HCl without filtering, add a few drops of pure ferric chloride solution and reprecipitate with NH_4OH). Boil for a few minutes; filter and wash the precipitate thoroughly with hot H_2O. If necessary, evaporate the filtrate to 175-200 cc. and make ammoniacal (about 1 cc. NH_4OH); boil gently and add slowly with constant stirring 10 cc. of a saturated ammonium oxalate solution; cover and let stand 2 hours or longer on a steam bath or in a warm place. Quantitatively wash solution and precipitate into a 250 cc. volumetric

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flask; cool to 20°-25° C.; fill to mark with distilled H_2O and mix thoroughly. Filter through quantitative paper making sure that filtrate is absolutely clear. Pipette an aliquot equivalent to 2 grams of the original leather and dilute to about 150 cc. Make slightly acid with HCl (methyl orange); cool if necessary; add a slight excess of clear saturated sodium ammonium hydrogen phosphate solution (5 cc. generally sufficient); while stirring vigorously, add a few drops of NH_4OH just until precipitation starts or until faintly ammoniacal; let stand 15 minutes; add with stirring 5 cc. concentrated NH_4OH; cover and let stand overnight at room temperature and proceed either by the gravimetric or volumetric method.

Gravimetric: Filter through a well prepared Gooch; wash the precipitate free from chlorides with 1 part concentrated NH_4OH sp. gr. 0.90 to 9 parts H_2O; finally just moisten the precipitate with a few drops of a solution of approximately 50 per cent NH_4NO_3 in 1 to 9 ammonia water; dry; ignite gently at first, then cover the crucible and ignite intensely for 20-30 minute intervals until constant in weight; weigh as $Mg_2P_2O_7$; multiply by factor to convert to $MgSO_4.7H_2O$ and express as per cent on 2 grams of leather.

Volumetric: Filter clear, through close quantitative paper; wash the precipitate free from chlorides with 1 part concentrated NH_4OH sp. gr. 0.90 to 9 parts H_2O; remove excess of ammonia wash water either by washing 3 or 4 times with neutral 60 per cent by volume methyl alcohol solution; or by spreading out the filter paper with its precipitate on to coarse absorbent filter paper for a couple of minutes and then on to a watch glass and dry for 1 hour at 50° C., (if 60° C. is exceeded, determination must be discarded); or by air drying the opened out filter with its precipitate overnight at room temperature. After removal of ammonia transfer paper with its precipitate to a beaker or flask; moisten with H_2O; thoroughly disintegrate the paper; add an accurately measured excess of standardized N/10 H_2SO_4 and 2 or 3 drops of methyl orange 0.1 per cent alcoholic solution). Dilute to about 100 cc. and determine excess of acid by titrating with N/10

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NaOH to a clear yellow without any suggestion of pink. One cc. of N/10 H_2SO_4 is equivalent to 0.0123 gram $MgSO_4.7H_2O$. Calculate to grams $MgSO_4.7H_2O$ and express as per cent on 2 grams of leather.

H. C. REED, *Secretary*.

The following method for the Melting Point of Greases (Other than Paraffine Wax) Thermometer Bulb Method, has been adopted by the Association as a provisional method:

MELTING POINT OF GREASES (OTHER THAN PARAFFINE WAX)

Thermometer Bulb Method

Dip a thermometer having a bulb not less than 5/8-inch nor more than 3/4-inch long, into the melted grease to the depth of the bulb, the grease being at a temperature approximately 10° above its melting point. Allow the thermometer to remain in the grease 5 seconds, remove, rotate slowly in a vertical position, and before quite solidified, remove excess drop of grease on bottom of bulb by touching to the hand.

After standing over night, place the thermometer in a test tube 6 inches x 1 inch, and cork lightly so that the bulb is 1 inch from the bottom of the tube. Suspend the test tube and thermometer in a beaker of water, the bottom of the test tube being about 1 inch above the bottom of the beaker. Place a flame underneath, and gradually raise the temperature of the water to about 15° below the probable melting point, and then raise the temperature not less than 1° nor more than 1½° per minute, until a drop of clear grease forms on the bottom of the bulb. This temperature represents the melting point.

The Centigrade thermometer shall be used.

H. C. REED, *Secretary*.

TIME REDUCTION IN THE TANNING PROCESS*

By R. O. Phillips

In selecting a subject for a paper to present at this meeting, I tried to choose a theme in which we are all interested—tanners as well as chemists. In talking upon a subject of such broad scope

* Read at the 19th Annual Meeting of the A. L. C. A., at Bigwin Inn, Canada, June 22, 1922.

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I will confine myself to the actual tanning operation, which will not include the preparation of the hides for the tan liquors or the finishing of the leather.

For over one hundred and fifty years, considerable attention has been given to the shortening of the tanning process, and with a good measure of success, when we consider that it required 1-3 years in earlier days to tan sole leather. Average American sole leather is now tanned in 80-120 days; English sole leather 90-150 days; and on the continent of Europe 28-120 days, depending whether partly or wholly drum tanned. I am, of course, speaking about the straight vegetable tannages.

In a book by Lalande "The Art of the Tanner," published in 1764, he suggested means to shorten the time of tanning, by the use of heat, extracts, and alum.[1] In 1777 Preiffer announced that he could tan sole leather in 6-8 weeks without vegetable tannin. He used the middle boiling fractions of coal tar containing phenols, xylenols and other hydrocarbon derivatives. From this time to the present day new tanning agents and improved tanning machinery have been developed which shorten the time of tanning.

Manufacturers of leather realized early that a shorter method would mean increased profits through greater production when business was good, a quicker turn-over, and a smaller outlay of capital. By shortening the process another important advantage is gained, in that the market and its requirements can more easily be followed. With a six months' tannage it is difficult to anticipate the amount and quality of leather that will be in demand so far ahead. Regulation of supply to fit demand is made much easier the shorter the tanning process, and the tanner would avoid to a great extent large warehouse inventories and at the same time have finished material when the market demands it. These are some of the things that make a short tanning process desirable, and I might say that part of the success of chrome tannage is due to these reasons. To produce as good a quality of leather has been the shortcoming of the majority of the ultra-rapid tanning processes.

[1] *J. A. L. C. A.*, 12, p. 142, 1917.

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In order to decrease the time of tanning it is necessary to increase the rate of diffusion of the tanning medium through the hide, which may be accomplished by chemical or physical means. The hide may be changed to permit faster penetration, the liquor may be altered to diffuse more rapidly, or some other influence such as heat, electricity, or other medium may be employed.

One of the fundamentals, perhaps the most important in a quick tannage, is the physical-chemical condition of the tanning medium. This may be influenced either from within or from without the hide. Tanning solutions may be either crystalloidal or colloidal or a mixture of these two states. Crystalloids diffuse rapidly through hide substance, while colloids diffuse much slower, depending probably to great extent upon the degree of the colloidol condition and the difference in electrical potential between the hide substance and the tannin. Examples of rapid crystalloidal tannage are the mineral tannages such as chrome, alum, etc. Vegetable tannages fall into the realm of colloidal penetration, and the speed of the diffusion may depend largely upon the degree of colloidality. If a crystalloid is added to a colloidal tan liquor, the penetration usually goes on much faster through the hide substance, whereas if a highly colloidal substance, such as some of the soluble vegetable gums is mixed with the tan liquor a restraining effect is usually produced and the penetration goes on much slower. Practical examples of the speeding up of penetration is the addition of sodium bisulphite to quebracho extract, while the effect of mixing colloids of high colloidal degree with tanning extracts of lesser colloidal state to retard diffusion is the subject of several patents dealing with the use of starch,[2] tragasol, etc.

The tanning medium no doubt is sometimes in actual molecular solution and able to penetrate the hide rapidly. The influence of the non-tannins has already been the subject of discussion[3] and no doubt the effect which the non-tannins have on the speed of penetration depends upon the nature of the non-tannins. It has been shown that the tannin particles have negative electrical charges and that the hide in acid solution is positively charged.

[2] British Patent. 110.470, 1917.
[3] *J. Ind. and Eng. Chem.*, 14, p. 45.

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If the tanning solution is made alkaline the hide becomes negatively charged and tanning cannot occur. From this it is seen that the difference of potential between the hide and the tannin affects the speed of tanning. This is one of the reasons a tan liquor of high acidity increases the tanning speed within limitations.

The simplest tanning process, if it can be called such, and one of the fastest is where the hide is "tanned" by merely drying, pliability being maintained in the finished product by keeping the hide in motion while the drying takes place. This is not true tanning as we usually think of the tanning operation, but the leather thus made is more resistant to the action of water and decomposing agents than the original wet pelt. The action is permanent to some extent for on wetting back skins once dried they never quite return to their original condition. An example of this "tannage" is the footwear of some savage tribes who draw the fresh hide over their feet and obtain perhaps a more completely tanned product by the alternate drying and wetting incurred during exposure to the weather.

The use of mechanical contrivances such as paddles, drums, rockers, wheels, etc., have done much to decrease the time of tanning. This is particularly true with the straight vegetable tannages. Drum tannage came out about 1890 when Durio invented his first successful quick process. Vegetable heavy leather which was formerly tanned in 1-2 years was tanned in 4 weeks by the drum process in some parts of Europe. In this country drums and paddles are extensively used in split leather manufacture. Vegetable sheepskin tannage which requires 8-10 days in pits is now largely tanned in drums in 3 or 4 hours

One of the most important changes which the tanning industry has undergone, is the introduction of new tanning materials some of which have speeded up the time of tanning greatly. Before going on with the vegetable tanning materials, which is the main subject of this paper, I will mention a few of the rapid tannages other than vegetable.

In 1853, Cavalius attempted to tan skins with potassium dichromate and then to reduce them in a bath of ferrous sulphate. Although leather was made, the process at that time was not a

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commercial success. In 1884 Schultz patented the two-bath chrome tanning process with which you are all familiar. For some years a large part of the world's production of upper leather has been tanned by the one or two bath rapid chrome process. It is needless to mention that certain classes of leather when tanned in chrome liquors have advantages. The element of time saving is not as important in tanning light leather as in the manufacture of heavy leather.

Within the last few years much attention has been given to iron tannage. The principal criticism of iron tannage is that it produces a dark color and a brittle grain, and in spite of the low cost it has not as yet attained any commercial importance. It has been suggested that a mixed tannage of chrome and iron be used to reduce the tanning cost, but of course the use of iron would preclude the use of vegetable tannin in the same leather unless a dark color is desired.

Aldehyde tannage has been known many years, is rapid, but the leather produced is poorly filled and becomes brittle with age. One theory of aldehyde tannage is that a polymerized or conjugated compound with hide substance is formed which renders it insoluble in water. Formaldehyde has been used as a tanning agent in connection with dehydrating salts, vegetable, chrome and alum tannages. Oil tannages, some of which are not very rapid, may be closely related to the aldehyde tannage. One theory is that the easy oxidizing oils give off acryl aldehyde. We are not sure, however, as to just what the tanning effect of the unsaturated oils is due for, as Meunier points out, a quinonoid structure may be formed by the oxidation of the oils.

Silicate tannage discovered by Hough offers possibilities, but up to the present time experiments show that the leather does not age well, probably due to the action of the silicic acid on the fibre. Leather has also been made by the "sulphur" tanning process, which consists in subjecting the skins, after pickling, in a concentrated solution of sodium thiosulphate, after which they are usually retanned with a light chrome or vegetable tannage. Encouraging experiments have been made in tanning leather through the use of the salts of zinc, tin, nickel, cobalt, aluminum, molybdenum, tungsten, uranium, cerium, manganese, bismuth, and the halogens. All of these processes are fairly rapid, which is what might be

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expected from the crystalloidal or low colloidal degree of the tanning substances. None of them has been commercially successful, however, either on account of the poorer quality leather produced or increased cost of tanning.

Of much scientific interest are the researches on the quinone tannage, on which Moeller, Meunier and others have worked. One of the most perfect leathers is produced by quinone, but its price at present makes its application commercially impossible. Quinone leather will stand the boiling water test and may be rapidly tanned in a weak solution of the substance.

The use of the synthetic tannins accelerates to some extent the tanning process. Straight synthetic tannages are indeed rapid but the quality of the leather is either very poor or the price of the extracts so high as to make their use alone impossible. The synthetic tannins which are being marketed to-day may be divided into two divisions, (1), those which tan and change hide substance into leather, (2), those which do not tan but rather have in some cases a solvent action on the hide itself. There are various mixtures of these two main divisions. The first class can be used alone, while the second class, having no tanning effect, can not be used alone. Both are usually blended or used in conjunction with the vegetable tannins; the first class, to give certain characteristic properties to the leather, usually light leather; to increase penetration, or as mordants for chrome and vegetable leather; the second class, to increase the rate of diffusion of the tannins through the hide substance, usually heavy leather; as a bleach, or to give better weight with certain materials in the extract wheel. There may be other applications of synthetic tannins which I will not take the time to go into here. All of the synthetic tanning substances which I have examined partly on account of their acidity and high degree of dispersion increase the rate of diffusion of vegetable tannin into the hide markedly when used in the tan liquors. If a synthetic extract is to be used great care should be taken in the selection of the product for there are some very poor synthetic extracts on the market.

Vegetable tannage dates back to the pre-historic period and is one of the oldest of industries. Chemistry and research have not developed any substance which will commercially and practically replace vegetable tanning materials for the manufacture

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of most kinds of leather. By far the greater part of the world's leather is tanned in vegetable liquors and in my opinion it will be many years, if ever, before vegetable tannin will be replaced to any great extent in the manufacture of heavy leather. It will be very difficult to produce a tanning material which will give equally good properties to heavy leather as given by the vegetable tannins at as low a cost of production.

The modern tendency has become more and more to shorten the process as much as possible in the tannage of almost all classes of vegetable tanned leather. In this country the use of extract wheels in heavy leather tanning began about 1902. This reduces the tanning time, since the wheel now drums in in a short time the weight which formerly took weeks in layaways or "vatting" pits. Extracting is one of the causes of the difference in time between American and English sole leather tannage, for in England extracting in wheels is not in general use, the "vatting" process in which the goods are immersed usually in bisulphited liquors at 90-100° F. and sometimes higher, being the general practice in heavy leather tanneries.

Drum tanning has become very popular on the continent of Europe since 1900 where it is the usual practice to strike through in pits and finish in drums, while some tanners tan heavy leather wholly in the drums. The process has been tried by several tanneries in America without much success although I understand that a part drum tannage of heavy leather is being used now by one or two tanners here with fair results. In our country and in England the result has been in most cases a much lower yield in the drum tanning experiments made than that obtained in the usual vat process. In heavy leather drum tanning an extract should be selected which is fairly high in insolubles when cold, and quite soluble when warm, which will, when the leather is cool precipitate the insolubles and give as far as possible the needed solidity and weight which drum tanned heavy leather usually lacks. Drum tannage of light leather is now very extensively practiced here.

For most kinds of heavy vegetable leather, however, the old lengthy process seems very difficult to supplant. Perhaps time is one of the fundamentals in the tannage of heavy leather, which is necessary in order to produce a high quality product. Up to

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the point where the hide is colored through most of the tannin which has been absorbed by the hide will have combined with the fibre and there is very little matter which can be washed out with water. From this point on, however, the tannin which is absorbed is not all taken up in combination with the fibre and increasing amounts are water soluble. After the hide is struck through the tanning solution within the hide is almost of the same concentration as the solution outside of the hide and both are nearly in equilibrium. In drum tannage due to the working of the hides the fore tannage is accomplished in less time and the after tannage or equilibrium of the extract within and without the hide is accomplished rapidly. If this were all that is necessary, drum tannage would be very successful, but something else takes place in long time tannage that does not to any extent in drum tannage.

If a clear tanning extract solution is allowed to stand for a long period of time a deposit or bloom usually appears, the kind and amount varying with different tanning materials. In the long time tanning process a deposition or bloom occurs within the leather which does not take place to any extent in the quick drum tannage. This deposition or precipitation of insoluble matter within the leather in the case of the long time tannage gives solidity, weight, firmness and water-proofness, which is one of the principal causes for the difference between the quick tanned and slowly tanned vegetable leathers. It is due to this fact that drum tannage of sole leather has failed more or less in this country, I believe, together with the looser fibre and structure occasioned by the bending of the hides within the drum.

A system of tannage which is new and which has met with considerable success in several large yards in America uses the principle of a fore or preparation tannage with a mineral salt in order to protect the grain, such as the reducing of a chromic salt in the hide by a cheap reducing agent. This prepares and plumps the hide in such a way that a strong tanning extract of between 80-120° Barkometer can be used at once, striking the leather through in a few days. This tannage produces an excellent quality of leather of good color, weight, plumpness, solidity and grain, and requires less than one month. I have had occasion to observe this process and have seen the leather in the dif-

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ferent stages of manufacture. It commends itself to me as being one of the best accelerated tannages yet developed. The finished leather by this process has all of the characteristics of straight vegetable tanned leather and wearing tests show it wears equally as well as straight vegetable leather.

For many years it has been known that by means of the electric current the vegetable tanning process can be shortened. The first use of electrolytic means for a quick tanning process was made by Crosse in 1849, who placed electrodes of zinc and lead in an ordinary pit.[4] In 1874 de Mertass of St. Petersburg designed an electric tanning process which was used in some 600 pits for a number of years. If two electrodes be placed in a cell between which are situated one or more hides, and the electric current admitted, the tannin being negatively charged, will migrate to the anode and is carried through the hide or to the point in the hide where it combines with the hide substance. If the hides in the cell completely separate the cell into two parts the phenomenon of electrophoresis takes place and there is a volume change of the liquor to the cathode side. A small amount of electrical energy gives a great increase in the diffusion of tannin through hides. Up to the present time electric tanning has not been successful on a commercial scale for the following reasons:

1.—The quality of leather has not been as good as that obtained by a long vat tannage unless the electric process be used solely as a fore tannage. If the leather be wholly tanned in the cell the degree of tannage is low and the leather is not well filled.

2.—There is precipitation of insoluble matter on the cathode side of the cell and decomposition of tannin on the anode side which until recently have not been overcome. The alternating current reduces precipitation and destruction of tannin to a minimum, but for certain reasons the alternating current itself has disadvantages. The electrical process is a very rapid one and I would not be at all surprised to see electricity play a part in the tanning of leather at some future date.

[4] *Jour. Soc. Chem. Ind.*, 32, p. 633, 1913.

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The vacuum process has been used with some success to accelerate the vegetable tanning process, especially during the war when a plant at Sireuil, France, employed the Nance vacuum process.[5] During the war large quantities of leather were made for the French Army by this vacuum process. The slowness of the long time tanning operation is partly due to the presence of air and water in the skins which prevents the penetration of the tanning liquors. By applying a vacuum these two impediments are removed to a great extent. In the plant at Sireuil the tanning was carried out in a series of autoclaves each of about 100 hides capacity. After the untanned hides are adjusted the autoclave is first evacuated and then a very weak spent liquor run in and left about twenty-four hours. This is then drawn off, the autoclave evacuated again and a 21° Barkometer liquor run in and left 4 days. This process is repeated with a 35° Barkometer liquor and left for 5 days, when the cycle is again accomplished with a 50° Barkometer liquor for 5-7 days. Sometimes a liquor as high in gravity as 90° Barkometer may be used according to the quality and type of leather being tanned. The spent liquors from each autoclave are used in the next lower one. For medium weight hides complete tannage is made in about 15 days. I understand that the leather is not as well filled and has a lower degree of tannage than that tanned by the longer process. There is one tannery in the States using the vacuum process.

When in England this past winter I had the pleasure of visiting a tannery which was tanning what appeared to be good sole leather in a two weeks' tannage. The whole process from the time the raw hides enter the tannery to the shipment of the finished leather occupies only one month's time. One week is consumed in unhairing and preparing the hides for tanning and one week to finish the leather after the two weeks' tannage. The tanning is accomplished for the first few days in pits until colored slightly, when the hides are removed and placed in a Wilson or other patented tanning wheel. The extract in these wheels is kept hot and is increased in strength as the tanning proceeds. In finishing the leather tunnel dryers are used and the drying operation is controlled automatically by several devices which

[5] *Chem. Abst.*, 14, p. 1061, 1920.

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keep the temperature and humidity absolutely constant. The leather that this concern is turning out is said to be very excellent as regards degree of tannage, weight, firmness and color.

There has been some research done, particularly in Europe, on a quick vegetable tannage through the use of highly colloidal substances, which although they restrain penetration, act in such a way that they permit the use of very strong liquors, so that a rapid tannage is possible, especially in drums. When used in drums the amount of restraining colloids is adjusted to prevent case hardening and yet through the drumming effect a quick tannage is obtained due to the high concentration of the tannin in the tanning extract colloid complex.

During the war Prof. Proctor mentioned a quick method of tanning[6] and which is as follows: Butts were taken from the handlers only just struck through, and after draining were laid flesh upwards and thickly coated with a mixture of strong hemlock extract and fine powder of divi-divi. The mixture is pasty and is laid on ⅜ inch to ½ inch thick. The goods are laid flesh to flesh and divi-divi chaff or ground bark containing not much tannin is put between the grain sides. The stacks were made into piles about twenty butts high where they are allowed to remain two or three days. They are then put down in a strong liquor and allowed a layaway of one to two days, when they are washed free of paste and finished in a clean light liquor such as myrobalan, and shedded. I do not know whether this method of shortening the usual vegetable heavy leather process is in use now or not.

Numerous other quick vegetable tannages have been suggested, such as the use of compressed air,[7] making the skins neutral before tanning,[8] use of various solvents,[9] etc., none of which have met with any real commercial success.

Probably no other problem in connection with tanning, perhaps outside of the researches on new tanning materials, has been given as much time and attention as has the question of

[6] *J. A. L. C. A.*, 10, 1915.
[7] British Patent, 140,092, 1920.
[8] *J. A. L. C. A.*, 9, p. 564, 1914.
[9] German Patent, 253,171, 1910.

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reduction in tanning time. Considerable progress has been made but it remains for the chemists and tanners of the future to develop an ultra-rapid process which will produce leather of as good quality as produced at the present time by the longer tannage. Such a rapid process would allow the market and its requirements to be more easily followed, and would do much towards stabilizing the tanning industry.

TREATMENT OF TANNERY WASTES TO PREVENT STREAM POLLUTION *

By E. B. Besselievre[1]

The disposal of the liquid, or semi-liquid wastes from tanneries is a problem that in a great many cases causes as much trouble and annoyance as any of the difficulties met with in the productive departments of the plant. Handling or treatment of such wastes is not usually taken up voluntarily by the tanners unless there is some economic purpose or commercially valuable product to be derived from such measures. Ordinarily it is because of some outside influence, usually local or governmental health authorities, that they become interested in learning of that system of treatment, which will, with the least initial expense give the results required. It is, therefore, the object of this paper to present briefly the salient points of the problem itself, and to explain how the problem has been met at a number of representative tanneries with satisfactory results and to illustrate with some lantern slides the several units of these plants and explain their principles of operation.

Almost without exception tannery wastes are discharged into nearby streams or other large bodies of water, or into the sewer systems of municipalities. As these wastes contain large percentages of solids, such as dirt, hair, lime, bits of flesh, leather scraps, etc., besides the various tanning process liquors, they are highly polluting, inimical to fish life close to the outlet, and are the cause of frequent stoppages in sewers and objectionable conditions on stream banks and beds. The problem, therefore, is to eliminate these solids to as great a degree as is economically practicable,

* Read at the 19th Annual Meeting of the A. I. C. A., Bigwin Inn, Canada, June 23, 1922.

[1] Sanitary Engineer, The Dorr Company, Engineers, New York.

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and to render the effluent safe to discharge without fear of complaint. This may be accomplished in one of two general lines of treatment, depending upon the ultimate condition of the effluent required. One method removes the coarser and settleable solids to a high degree. The other not only removes the coarser and settleable solids, but by means of chemicals causes the precipitation of the very light solids, eliminates any color and neutralizes the effluent, and possibly employs disinfection of the final effluent for entire elimination of pathogenic bacteria.

The degree of treatment required and the character of the waste to be treated are the determining factors in the selection of the method and the design of the proper plant. In those cases where the tannery waste discharges into a sewer system, which in turn empties into a stream or large body of water not used for potable purposes, or where the discharge is directly into these bodies of water, the usual maximum treatment required is that the tanneries so discharging clarify their wastes to the extent of removing the greatest practicable percentage of solids in order to prevent deposition and clogging in the sewers, or collections of solids in the body of water. On the other hand where the tannery waste is turned into small streams that are used for potable purposes or as fishing grounds, a higher degree of treatment is required to produce a final effluent that will not pollute the waters. As in the first instance, the removal of the solids is an essential preliminary treatment, but the process must go further and by the addition of chemicals cause the precipitation of the finer solids and soluble matters, and in some cases it may be necessary to provide filters of sand or stone and finally to thoroughly disinfect the effluent by liquid chlorine or other bacteria destroyer. Usually, however, where treatment other than sedimentation is required, the addition of a precipitant previous to the sedimentation tank with chlorination of the effluent will suffice.

In Peabody, Mass. and in Newark, N. J., large separate sewers have been built by those municipalities especially to carry the wastes from a large number of tanneries. In Peabody several of the tanneries have installed individual treatment plants for their wastes before emptying into this sewer, and in Newark it is planned to combine the wastes from a group of tanneries and treat them all in one plant previous to entering the sewer.

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In the past, several methods of treating tannery wastes have been employed with indifferent success. These methods have usually been crude screening units requiring much manual attention to remove the screenings from the screen, or settling basins which periodically had to be shut down and the accumulated mass of solids dug out by hand. In these plants a great amount of manual labor was necessary to maintain the plant in any kind of operating condition, duplicate units of screens or settling tanks were required, or else the entire flow had to be discharged untreated while the screens and tanks were being cleaned. This duplication increased the initial cost of the plant and the method of operation made the running expense inordinately high. The effluents from the plants were subject to great and serious fluctuation in clarification and the worst condition of effluent was as likely to happen at the worst time as not. Again the plants were unsightly and not one of the show parts.

A system which has been used successfully at several tanneries for some time for removal of the solids from tannery waste, is one comprising two mechanical units, each adapted to its special function and possible of use either singly or in combination, as the degree of treatment required necessitates. These units are, first, a revolving mechanical screen unit, for removing the coarser solids, such as hair, leather scraps, fleshings, etc., and the second a sedimentation unit equipped with mechanical means for collecting the finer and lighter solids which, with quiescent settling will fall to the bottom of the tank in a reasonable period of say, two or three hours. The important features of these two units are that they are mechanically simple and rugged in construction, therefore not subject to breakdown or repair. As these units mechanically accomplish the removal of the solids from the waste and their collection and placement into the receptacle in which they are removed to the point of final disposal, skilled mechanics are not required to run the plants and replies to a questionnaire indicate that two hours' attention per day is an average.

The revolving screen unit is unique in that it is self-cleansing, that is, it does not require any brushes, scrapers or jets to remove the screenings from the screen plates. It consists of a perforated cylindrical drum, mounted on a horizontal shaft with the drum partially submerged in the flow of raw waste. The

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screened waste, after passing through the perforations into the cylinder, flows out through a discharge opening provided in one end of the drum. An effective seal around the discharge opening prevents unscreened waste from by-passing the screening medium. The combination of the design and action of the screened effluent inside the drum cause a spouting action which positively cleans the screening medium and at the same time deliver the screenings into the screenings pit. Where coarse, bulky solids are to be removed, such as in tannery waste, a lifting fin ejects these solids into the screenings pit. Perforated plate or wire mesh screening mediums are used in each installation according to local conditions. Screenings are removed from the pit by means of a dewatering and elevating mechanism which collects the screenings and carries them in perforated receptacles to a point convenient for emptying into cans or carts, in a condition making them easily transported to point of final disposal. Tests made at plants where these screens are in operation on tannery wastes show removals of 16.3 per cent of the suspended solids, with one-eight inch perforations. To put this into comprehensive figures, one plant produced from a volume of 423,000 gallons of waste per day a daily average of 30,000 pounds of wet screenings, that is, with a moisture content of about 85 per cent. These screenings are mostly hair.

The second unit, for the collection of the finer and lighter solids, lime, etc. is known as the Dorr Sewage Clarifier, which is a combination of a sedimentation basin and a mechanism for the continuous collection and removal of the settleable and suspended solids from tannery wastes in the form of a sludge. Its essential features are roughly as follows: The wastes are fed into the Clarifier inside a circular baffle extending below the liquid level. The incoming stream tends to diffuse over the entire area and the solids settle at the bottom of the basin over which, by a combination of flow and sweeping, they are conveyed to a common point for discharge. The entire area of the bottom of the basin is swept with each revolution of the mechanism, the four radial arms of which, equipped with plows set at an angle with them, sweep the floor of the tank, collecting and partially dewatering the sludge by compression and carrying to the point of common discharge. From this point the sludge can be withdrawn, either

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through the tank bottom or from above the center of the tank. In cases where the sludge is to be taken out upwardly, the Clarifier is equipped with a central upward discharge well. This well revolves with the mechanism and the sludge pump suction extends to within a few inches of the bottom of the well. When sludge is being withdrawn the sludge level in the well is usually about 12 inches below the liquid level in the tank. It is this difference in head which forces the sludge up into the well where is can be reached by the pump suction. The clarified liquid overflows a peripheral weir into a collecting channel whence it gravitates from the treatment plant.

The size of the Clarifier unit is dependent upon the rate of flow, the character of the waste to be handled, that is, percentage of solids, and upon the desired degree of clarification. The sedimentation units are in all cases comparatively shallow, averaging 5 to 7 feet at the periphery and having a slight slope to the center. In cases where the wastes must be pumped to the treatment plant the Clarifiers may be built entirely above ground, in which case the cost of construction is materially reduced and the plant made very neat in appearance as well. One of the important features of the Clarifier which tends to reduce the initial and operating costs of a plant is that due to the method of continuous sludge collection and removal from the tank, it is not necessary to provide duplicate units. Thus there are no accumulations of sludge in the Clarifier, and consequently, no reduction of the volume of the tank and the following deterioration of the effluent due to the carrying over of solids by the increase in velocity over the discharge weir. In the Clarifier the velocity of flow over the peripheral weir is low and constant.

Removals of suspended solids from tannery wastes by the Clarifier as recorded in tests on operating plants have been as high as 65 per cent of the suspended solids remaining in the wastes after passing through the screen unit, which has removed the very coarse solids. Total plant removals where the two units referred to have been used, approximate an average of 70.9 per cent. At one plant the sludge from the Clarifier amounts to an

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average of 19.8 tons of wet sludge per day from a flow of 423,000 gallons. This sludge has an average moisture content of 91 per cent.

The combination of these two units provides a plant that will deliver an effluent of uniform clarity, and which may be discharged into sewers or streams without fear of clogging or of troublesome collections on stream beds or banks. If removal of color, or dissolved solids is necessary, precipitants are easily added to the waste prior to its entrance into the Clarifier, and the resultant precipitation is taken care of by the mechanism. Where disinfection is also required, the effluent from the Clarifier may be very readily treated with liquid chlorine or other forms of disinfectant. Up to the present time some fifteen tanneries in all parts of the U. S. have adopted one or both of these units for handling their wastes, and the plants are in daily operation.

While attempts have been made to produce a fertilizer from tannery sludges and screenings, up to the present time there has been no great success achieved, but at any time that such usage of tannery wastes by-products should be evolved, the screening and sludge from the units described would be more valuable and less costly to transform into fertilizer than other sludges because of their lower moisture contents.

At one plant, the screenings which are mostly hair, are sold to a local felter and mattress maker for about $3.00 per ton, and while this does not entirely pay the cost of operation of this particular plant, it comes close to doing so. During the war this same tannery sold its screenings at times for $25.00 per ton and during this period the treatment plant more than paid its own way. Records of operation from two plants handling large volumes of tannery waste show that the daily costs of operation are small, consisting entirely of the electric current used, and the time of a man a few hours a day. One plant, with a volume of 423,000 gallons per day shows a total cost of operation of $3.20, of which $1.20 covered the electric current and the balance for labor at 50 cents per hour. In another case with a volume of 800,000 gallons per day, the total daily expense was $4.67, of which $2.67 was for power and the balance labor at 50 cents per hour. These

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figures do not include the cost of hauling the sludge away, which is done only at intervals of three to four days in one plant and in the other the sludge is pumped direct to drying beds.

That the amount of ground space required for plants of this type is small may be gained from the fact that for a plant treating 100,000 gallons per day, with both units installed, the total area required is 778 square feet and for a million gallons per day the total area is 6,330. In the first case the area required is a small portion of an ordinary city lot and for the larger one about one-seventh of an acre will suffice.

While the plants do not require housing,, several tanners have enclosed their entire plants, while others have constructed large houses on the superstructure, but all that is necessary is to protect from the weather the driving unit, and a small house is amply sufficient.

THE PLUMPING OF HIDE POWDER BY LACTIC AND ACETIC ACIDS*

By J. S. Rogers

The researches of Procter, Wilson, Loeb, Smith, Porter, Atkin, and others have thrown much light upon the subject of the plumping of protein materials of the nature of gelatine and hide. The importance of the plumping power of tan liquors in the production of firm well filled leather has long been known. Until recently the only methods available for predicting the plumping power of tan liquors were those which gave a figure for the total acidity of the liquors. Procter's Lime Water Method, used by the European leather chemists, and the Gelatine-Hematine Method used by the American leather chemists, are representative of these methods. Although it had long been realized that the total acidity value did not give all the information desired concerning the plumping power of tan liquors, it was not until Wood,[1] Sand, and Law demonstrated the importance of the hydrogen ion concentration in these liquors, that chemists began to study these other factors which so materially affect the plumping power.

* Read at the 19th Annual Meeting of the A. L. C. A. at Bigwin Inn, Canada, June 23, 1922.

[1] Wood, Sand, and Law, *Coll.*, 150 and 432, 1911.

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Procter,[2] Wilson[3] and the more recent investigations of Smith[4] and Loeb[5] have shown quite clearly that when proteins are subjected to the action of acid or alkali solutions, that salts are formed which because of their ionization result in swelling the protein material. Porter[6] and Atkin[7] have demonstrated that hide in the form of powder reacts in practically the same manner toward acids and alkalies as does gelatine.

Measurement of hydrogen ion concentration, however, must not be expected to solve the plumping problem for the tanner. The effect of hydrogen ion concentration is considerably influenced by factors such as the repressing action of neutral salts and decreased swelling power caused by combination of hide and tannin. The swelling is not directly proportional to the hydrogen ion concentration even in the presence of acid alone. This has been shown by Loeb and Porter in cases when the maximum plumping has been reached and a further increase in hydrogen ion concentration causes a decrease in plumping.

A direct method for measuring plumping would be valuable to the tanner in detecting variations from normal plumping conditions in tan liquors. When such variations were detected it would then be necessary to investigate the cause, and from the data thus obtained determine what corrective measures must be applied. Before any direct measurement method can be intelligently applied it must be carefully studied and considerable data must be collected by use of the method under consideration upon solutions of known composition.

It is with a view to adding something to the data already collected along these lines that these results herein given are presented. Porter,[6] McLaughlin[8] and Claflin[9] have all used different methods for the direct measurement of plumping. In this work it has been decided to use a modification of the Claflin Method.

[2] H. R. Procter, J. A. L. C. A., 6, 270, 1911. *Koll. Chem. Beiheifte*, 2, 243, 1911.
[3] Procter and Wilson, *J. Chem. Soc.* (Trans.), 109, 307, 1916. J. A. L. C. A., 11, 261, 1916.
[4] C. R. Smith, *J. Ind. and Eng. Chem.*, 12, 878. *J. Am. Chem. Soc.*, 41, 135.
[5] J. Loeb, *Jour. Soc. Lea. Trades Chem.*, 5, 137, 146, 1921.
[6] E. C. Porter, *Jour. Soc. Lea. Trades Chem.*, 5, 259, 1921. E. C. Porter, *Jour. Soc. Lea. Trades Chem.*, 6, 83, 1922.
[7] W. R. Atkin *Jour. Soc. Lea. Trades Chem.*, 6, 138, 1922.
[8] Geo. D. McLaughlin, J. A. L. C. A., 15, 228, 1920.
[9] A. A. Claflin, J. A. L. C. A., 15, 234, 1920.

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A comparison has been made between the plumping action of lactic and acetic acids of the same normalities, also a comparison between the plumping action of lactic and acetic acids of the same calculated hydrogen ion concentrations given in terms of the p^H values. The effect of the presence of tannin has also been studied and some results have been obtained showing the effect of the time factor in the measurement of plumping. No experiments have been conducted in the presence of added neutral salts.

Procedure for Making Plumping Measurements

A flask graduated to deliver 200 cc. was filled to the mark with the acid solution to be used. This solution was then poured upon 5 grams of air dry hide powder in the shake bottle, the flask allowed to drain for about one minute, removed and set aside. The hide powder acid mixture was then shaken for ten minutes, then filtered through a 6-inch circular cloth folded and placed in a glass funnel and the filtrate collected in the same 200 cc. flask from which the acid solution has been poured. After nearly all the filtrate had run through it was poured back into the shake bottle to rinse out any adhering particles of hide powder. The final filtrate was collected in the original 200 cc. flask and the filter allowed to drain until drops ceased to fall. The 200 cc. flask was then filled to the mark from a pipette or burette and the volume in cc. which was required noted as the total volume of solution taken up by hide powder, shake bottle, cloth and funnel. From this volume the apparatus hide powder blank for water was subtracted to obtain the corrected volume absorbed, or the plumping due to the acid present. Air dry American Standard hide powder was used for all the experimental work. Determinations were made at laboratory temperatures which ranged from 25-28° C.

Blank determinations were made with the apparatus using water and no hide powder, in order to determine how much water was taken up by the apparatus used. The volume of water taken up by the shake bottle, funnel and filter cloth has been designated the "Apparatus Blank." This apparatus blank obtained as an average of ten closely agreeing determinations was 9 cc.

A series of blank determinations was then made in which 5 grams of hide powder were shaken with 200 cc. of distilled water.

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This blank was designated the "Apparatus Hide Powder Blank." The results of nine closely agreeing determinations gave 39.4 cc. as an average "Apparatus Hide Powder Blank." The average water absorption by 5 grams hide powder is, therefore, by difference 30.4 cc.

In Table I are given the results obtained when lactic acid was used in strengths ranging from 0.01 to 2 N.

TABLE I.—PLUMPING WITH LACTIC ACID.

Test No.*	Normality of acid	Volume absorbed Cc.	Avg. volume absorbed, cc.	Plumping due to acid, cc.
1	0.010 N	67.2 66.1	66.6	27.2
2	0.025 N	79.2 80.1	79.6	40.2
3	0.050 N	87.3 87.9	87.6	48.2
4	0.075 N	89.8 92.0	90.9	51.5
5	0.100 N	92.2 91.4	91.8	52.4
6	0.125 N	94.7 94.9	94.8	55.4
7	0.150 N	94.0 94.5	94.2	54.8
8	0.175 N	94.5 94.5	94.5	55.1
9	0.200 N	94.2 94.8	94.5	55.1
10	0.500 N	93.1 93.5	93.3	53.7
11	1.000 N	88.8 90.3	89.5	49.9
12	1.500 N	86.4 86.6	86.5	46.9
13	2.000 N	84.5 82.9	83.7	44.1

*Tests 1-9 in Tables I and II were run in two series and the apparatus hide powder blank was 39.4 cc.

*Tests 10-13 in Tables I and II were run at another time and the apparatus hide powder blank was 39.6 cc.

The volumes in the last columns of Tables 1-4 inclusive were obtained by deducting the apparatus hide powder blank for water from the total volume of liquid absorbed.

In Table II are given the results obtained when acetic acid was used in strengths ranging from 0.01 to 5 N.

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In Table III are given a few results which show the plumping action of U. S. P. tannin upon hide powder. These results have, in the last column, been corrected for the apparatus hide powder blank for water.

Merck's U. S. P. tannin was used in these tests. It showed upon analysis by the A. L. C. A. Official Method 84 per cent tannin.

TABLE II.—PLUMPING WITH ACETIC ACID.

Test No.	Normality of acid	Volume absorbed, cc	Avg. volume absorbed, cc	Plumping due to acid, cc.
1	0.010 N	48.9 49.5	49.2	9.8
2	0.025 N	59.6 58.8	59.2	19.8
3	0.050 N	66.9 66.8	66.8	27.4
4	0.075 N	71.4 69.4	70.4	31.0
5	0.100 N	75.1 75.5	75.3	35.9
6	0.125 N	78.0 76.5	77.2	37.8
7	0.150 N	78.0 78.8	78.4	39.0
8	0.175 N	79.4 80.2	79.8	40.4
9	0.200 N	82.1 82.7	82.4	43.0
10	0.500 N	90.2 90.6	90.4	50.8
11	1.000 N	94.6 93.7	94.1	54.5
12	1.500 N	95.0 95.6	95.3	55.7
13	2.000 N	95.6 96.3	95.9	56.3
14	5.000 N	91.6 91.6	91.6	52.0

Such amounts were weighed out as would give 0.5 per cent, 1 per cent and 1.5 per cent respectively of actual tannin on the basis of the above analysis.

TABLE III.—PLUMPING WITH TANNIN.

Test No.	Tannin per cent	Volume absorbed, cc.	Avg. volume absorbed, cc.	Plumping due to tannin, cc.
1	0.5	50.7 48.5	49.6	10.2
2	1.0	52.5 53.5	53.0	13.6
3	1.5	51.0 51.3	51.2	11.8

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In Table IV are given results obtained by treating 5 grams of hide powder with solutions containing 0.5 per cent, 1 per cent and 1.5 per cent tannin and which varied from 0.01 N to 0.10 N in lactic acid. These results have been plotted and are shown in Figure 3 with the curve for lactic acid without tannin.

TABLE IV.—Plumping with Lactic Acid in the Presence of Tannin.

Test No.	Per cent tannin	Normality of acid	Volume absorbed, cc.	Avg. vol. absorbed, cc	Plumping due to acid in presence of tannin, cc *
1	0.5	0.010 N	69.5	69.5	30.1
			69.5		
2	0.5	0.025 N	75.9	76.8	37.4
			77.6		
3	0.5	0.050 N	79.8	80.0	40.6
			80.3		
4	0.5	0.075 N	80.3	79.2	39.8
			78.2		
5	0.5	0.100 N	78.2	78.4	39.0
			78.5		
6	1.0	0.010 N	66.6	67.4	28.0
			68.1		
7	1.0	0.025 N	71.5	72.4	33.0
			73.2		
8	1.0	0.050 N	74.7	74.6	35.2
			74.6		
9	1.0	0.075 N	74.9	75.1	35.7
			75.3		
10	1.0	0.100 N	71.4	73.3	33.9
			75.2		
11	1.5	0.010 N	59.0	61.9	22.5
			64.7		
12	1.5	0.025 N	68.2	69.0	29.6
			69.8		
13	1.5	0.050 N	65.6	69.2	29.8
			72.9		
14	1.5	0.075 N	71.0	70.4	31.0
			69.8		
15	1.5	0.100 N	67.6	68.2	28.8
			68.8		

Plotting the plumping values shown in Tables I and II for lactic and acetic acids, using the volumes of solution absorbed as ordinates and the normalities as abscissas, the curves shown in Figure I, are obtained. As might have been expected the more highly ionized lactic acid showed greater plumping at the lower normalities than did the less ionized acetic acid. The maximum plumping was reached in the case of lactic acid at 0.125 N while for acetic it was only reached when the normality had been increased to 2 N. These curves show that these acids when used

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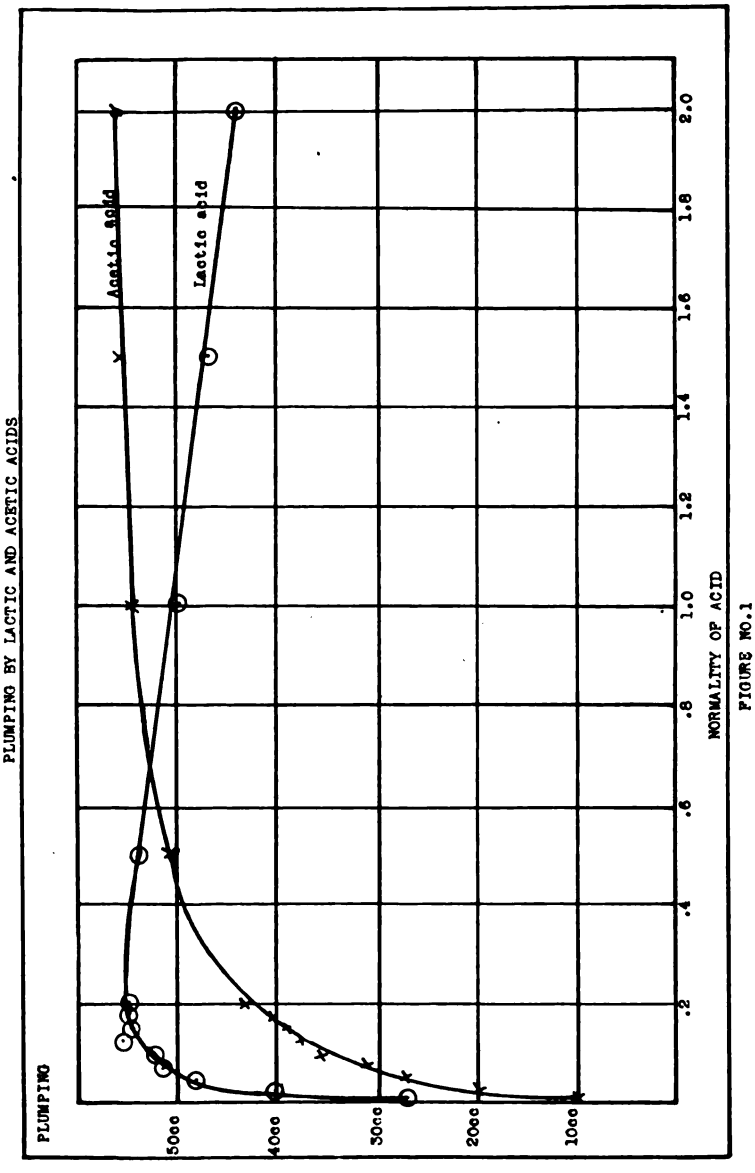

FIGURE NO. 1

in the same normalities exhibit marked differences in plumping power. This is in agreement with the fact already known that total titratable acidity is not a measure of the plumping power

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of a tan liquor. These curves indicate further that different acids of the same normalities and having different ionization constants will not exhibit the same plumping power.

In order to observe these results from another point of view, the plumping values obtained in Tables I and II have been plotted as ordinates against the calculated p^H values of the acid solutions used as abscissas. These curves are shown in Figure 2. The method of calculating the p^H values was as follows. Use

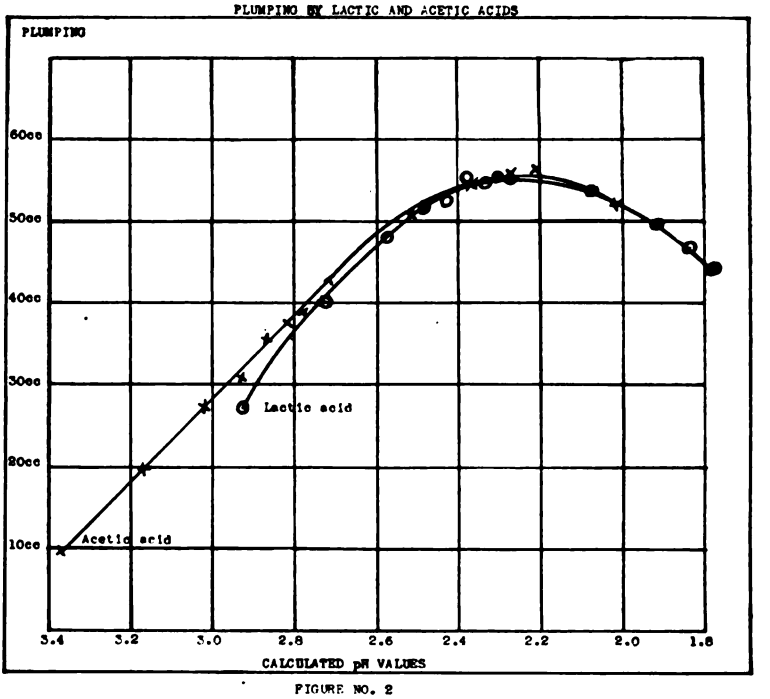

FIGURE NO. 2

was made of the equilibrium equation given by Clark in "Determination of Hydrogen Ions," page 29.

$$[H^+] = \sqrt{KaSa + \frac{Ka}{4}} - \frac{1}{2}Ka$$

when Ka is small in relation to Sa the above equation may be simplified to

$$[H^+] \propto \sqrt{KaSa}$$

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This form of the equation has been used for these calculations.

$[H^+]$ = concentration of hydrogen ions
Ka = ionization constant of the acid
Sa = total acid
Ka for lactic acid = 1.4×10^{-4} @ 25°C[10]
Ka for acetic acid = 1.86×10^{-5} @ 25°C[10].

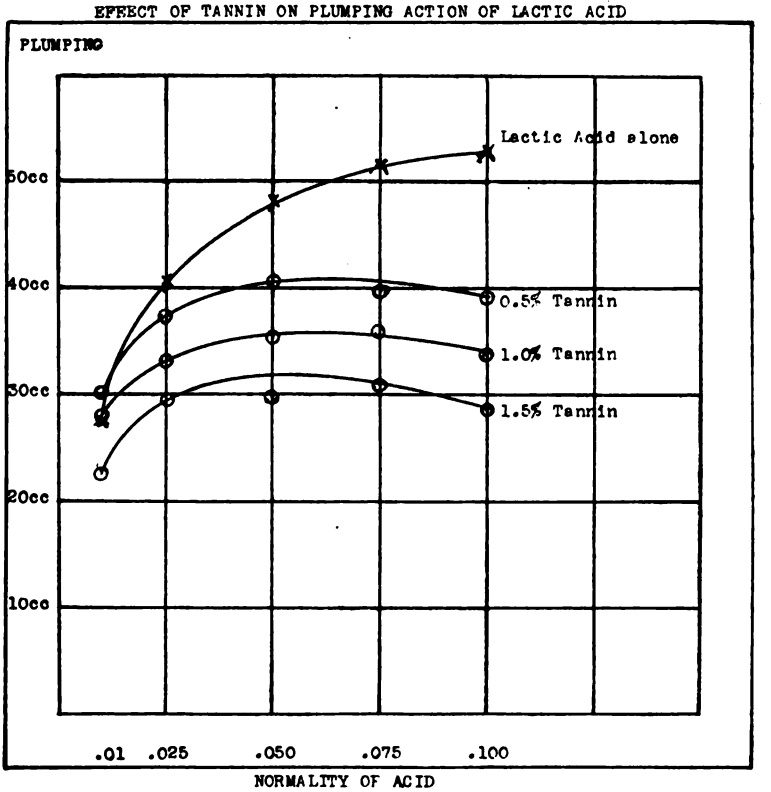

FIGURE NO. 3

After obtaining the hydrogen ion concentrations the p^H values were calculated by use of the equation $p^H = \log \frac{I}{[H^+]}$.

An examination of the curves in Figure 2 shows that the maximum swelling obtained by both acids is practically the same and that this maximum is reached at practically the same p^H value. It will be noted that practically the same swelling will result from acetic as from lactic acid, when used alone, if the hydrogen ion

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concentrations are the same. Attention is called to the fact that these calculated p^H values represent the solutions as added to the hide powder and not the solutions after being in contact with the hide powder.

These curves indicate that the maximum swelling for both lactic and acetic acids when measured by the above method is reached between 2.2 to 2.4 p^H. This is in reasonable agreement with the results of Porter for HCl which also has a monovalent anion. From the work of Loeb[5] we are lead to expect that the maximum swelling produced by different acids, having a monovalent anion, will be reached at practically the same p^H value.

Although tannin alone, as indicated by the results given in Table III, seems to show some plumping effect upon hide powder, the results given in Table IV show that tannin has a very marked depressing action upon the plumping caused by lactic acid. The question arises. Does protein-tannate exercise a repressing action similar to the action of neutral salts?

The calculated p^H values for acetic and lactic acids in the dilutions used have been assembled in Table V.

TABLE V.—CALCULATED p^H VALUES FOR LACTIC AND ACETIC ACIDS AT 25° C.

Normality	Acetic p^H	Lactic p^H	Difference in p^H	Difference in cc. plumping
0.010	3.37	2.93	0.44	17.5
0.025	3.17	2.73	0.44	20.5
0.050	3.02	2.58	0.44	21.0
0.075	2.93	2.49	0.44	21.0
0.100	2.87	2.43	0.44	17.0
0.125	2.82	2.38	0.44	18.0
0.150	2.78	2.34	0.44	16.0
0.175	2.74	2.31	0.43	14.5
0.200	2.72	2.28	0.43	12.5
0.500	2.52	2.08	0.44	2.9
1.000	2.37	1.92	0.45	4.6
1.500	2.28	1.84	0.44	8.2
2.000	2.21	1.78	0.43	12.2
5.000	2.02			

In Table VI are given some results which show how an increase in the time of contact effects the plumping. These results indicate that ten minutes' shaking is not sufficient time to bring the plumping reaction to equilibrium.

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TABLE VI.—PLUMPING WITH N/10 NORMAL LACTIC AND ACETIC ACIDS FOR VARYING PERIODS OF TIME.

(Results corrected for apparatus hide powder blank).
(The hide powder used for this series of tests was sieved through a 20-mesh sieve).

Time hours	N/10 lactic acid cc.	N/10 acetic acid cc.
4	57.8	41.5
12	62.6	46.0
20	64.9	48.9

These results here reported must be considered as comparisons made under certain fixed conditions. The method used is not recommended in its present form for use in control of tannery liquors. It is believed, however, that the data given will be of assistance in the development of a suitable method. An effort should be made to work out a method which will approximate plant conditions as regards proportion of hide to tan liquors, time of contact, condition of hide, etc.

A direct method of this type may readily serve as an indicator to show abnormal plumping conditions in tan liquors, and as such will be of greater assistance to the tanner than the determination of total acidity. When the cause of the abnormal conditions of plumping is sought, recourse must be had to other methods, and it is in such cases that total acidity, hydrogen ion concentration, neutral salt effect, etc., must be studied.

Reed and Blackadder[10] have suggested a change in the manipulation of the Claflin Method, which may result in a marked improvement in the operation of this method.* They state that the hide powder used is acid in reaction, and later state that it contains lime. It would appear that if the reaction of the hide powder is on the acid side of the isoelectric point that under such conditions the calcium present would be in the form of a calcium salt, and thus would exercise its repressing action when the hide powder was shaken in water in the blank determination. In the present work a correction for the apparatus hide powder blank for water has been made, and it is believed that this procedure has practically eliminated the influence of the salts and acid present

* In a later paper Reed describes further improvements upon the method. This paper was presented at the 1922 annual meeting under the title "The Versatility of a Plumping Method."

[10] H. C. Reed and T. Blackadder, J. A. L. C. A., 17, 109, 1922.

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in the hide powder. It is believed that an isoelectric hide powder for use as standard in plumping measurements would be highly desirable.

SUMMARY

The plumping action of varying normalities of acetic and lactic acids has been compared, and the results show that the same titratable acidity of these acids does not produce the same plumping.

A comparison of the plumping action of acetic and lactic acids of the same calculated hydrogen ion concentration indicates that the maximum swelling produced by these acids is the same and is reached at the same hydrogen ion concentration.

The presence of tannin lowers the plumping effect produced by these acids.

The Claflin Method has been demonstrated to be a workable method and after further improvement as to details of manipulation, should prove to be serviceable as a control method for the measurement of the plumping of tan liquors.

ANALYSIS OF SYNTHETIC TANNING MATERIALS—1922 Committee Report

T. A. Faust, Chairman

At a meeting of this Committee in New York, Sept. 13th, 1921, it was decided that the following three points would keep the Committee busy for the coming year:

(1) Determination of the amount of free sulphuric and free sulphonic acid present.

(2) The adaptation of the official method of tannin analysis to these materials.

(3) Determination of the free formaldehyde.

The questions of bleaching, plumping and solvent action were discussed, but were left over until later. The determination of the ash was deemed important, and was to be taken on immediately. The use of the hydrogen ion concentration apparatus for estimation of sulphuric and sulphonic acids was discussed by the Committee, as it was thought this method would distinguish between the two acids. However, the chairman made some inquiries during the year and concluded that in view of the status of this

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method, the complicated nature of the acids present, and the inapplicability of the method to the average laboratory, that the value of this procedure was rather doubtful.

A copy of the minutes of the above meeting was sent to each member of the Committee together with proposed methods of determining sulphuric and sulphonic acids by Dr. Hill and Mr. Kernahan. These were followed by further proposed methods for the same determination by Mr. Englund and Mr. Hayes. Criticisms of their methods were asked for. A number of real and theoretical objections were offered to all the proposed methods a digest of which was sent to all members. It was finally decided to submit Hills, Englunds and Hay's methods for actual work.

Four manufacturers, Barrett, Röhm and Haas, Klipstein and Yocum furnished large samples of their products for the use of the Committee. Samples of each of these were sent out numbered so as not to disclose the names of the manufacturers, and the Committee were asked to try out the three proposed methods, and to report their results and criticisms.

The following members served on this Committee:

Dr. J. B. Hill and G. W. Merryman.
C. C. Smoot, III. and L. E. Stacey.
A. A. Claflin.
J. S. Downing.
G. V. Downing.
L. H. Englund.
R. W. Frey and I. D. Clarke.
P. Hayes.
M. M. Kraft.
Dr. S. Kohn.
C. M. Kernahan and C. A. Blair.
Dr. T. Blackadder.
E. H. Klipstein.
T. A. Faust and L. G. Glass.

METHODS SUBMITTED.

Hill's Method

(1) A suitable sized portion of the synthetic tanning material is weighed out in a crucible, evaporated carefully to dryness and the residue moistened with concentrated sulphuric acid. The mixture is re-

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evaporated to remove the sulphuric acid and gently ignited to a dull red heat. During the ignition small granules of ammonium carbonate are added from time to time to assist in breaking up sodium pyrosulphate which is formed. The ignition is continued to constant weight, the residue being weighed as sodium sulphate. The size sample taken should be so adjusted that the weight of the ignited residue is about 0.2 to 0.5 gram.

$$\frac{\text{Wt. ash} \times 100}{\text{Wt. sample}} = \text{Per cent Na as } Na_2SO_4.$$

(2) A second portion of the material to be tested of such size as to give about 0.2 to 0.5 gram of barium sulphate is weighed out, dissolved in about 500 cc. of distilled water, acidulated with hydrochloric acid and precipitated by slowly adding a 3 per cent solution of barium chloride to the cold dilute solution with stirring. The precipitate is allowed to settle about six hours and is filtered cold. The precipitate is washed on the filter with cold water followed by hot water and hot dilute hydrochloric acid. The washed precipitate is dried, ignited and weighed.

$$\frac{\text{Wt. } BaSO_4 \times .4202 \times 100}{\text{Wt. of sample}} \quad \text{Per cent total } H_2SO_4$$

Per cent total H_2SO_4 — (per cent sodium sulphate $\times$ .6904) = Free sulphuric acid

Englund's Method

(1) Boil under reflux condenser with known quantity of N or N/2 hydrochloric acid. The solution is then titrated with N or N/2 NaOH and blank acidity due to HCl deducted and remainder calculated as sulphuric acid. This gives free sulphuric and (free and combined) sulphonic.

(2) Boil with an excess of CaO and some $CaCl_2$. Allow to stand in warm place for about an hour, filter and wash the precipitate.

(a) Determine SO_3 in filtrate by oxidizing with chlorine or bromine water or potassium chlorate, nitric acid, etc., and precipitate and weigh as barium sulphate. This gives *total sulphonic acid and sulphonates* in terms of sulphuric acid.

(b) Determine SO_3 in calcium sulphate precipitate by boiling with hydrochloric acid and some sodium chloride and precipitating as barium sulphates. This gives *total free sulphuric and sulphates*.

(3) Evaporate to dryness or to a syrup and leach out with ethyl alcohol which will dissolve the sulphonates and free sulphonic acids and combine with the free sulphuric forming $C_2H_5.H_2SO_4$ which is soluble. Pour off solvent and wash repeatedly with ethyl alcohol until neutral. If ammonia has been found absent, mix MgO or Na_2CO_3 with the residue, ignite and determine the SO_3 by dissolving melt in hot water, acidulating with HCl and precipitating with barium chloride. If ammonia be present destroy organic matter with sodium peroxide and determine SO_3 as barium sulphate. *Gives sulphates.*

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1. Free sulphuric — Free sulphonic — Sulphonates
2. (a) — Free sulphonic — Sulphonates
2. (b) Free sulphuric — Sulphates
3. — Sulphates

2b — 3 — 1 — 2a = Free sulphuric.
3 = 2b — (1 — 2a) = Free sulphates.
1 — 2b + 3 = Total sulphonic acid and sulphonates.

Hayes' Method

(A) A regular Procter and Searle determination which would give the total free acidity (sulphuric and sulphonic).

(B) A determination of the total sulphates (free sulphuric and sulphates) by precipitation as suggested by Dr. Hill.

(C) A determination of the sulphates by precipitation as above after driving off the free sulphuric acid at a low heat.

(A) Free sulphuric and free sulphonic
(B) Free sulphuric and sulphates
(C) Sulphates

B — C = Free sulphuric
A — B + C = Free sulphonic acid
C = Sulphates.

Theoretical Criticisms of Methods

Hill's Method

(1) Does not take into consideration volatile sulphates and possibility of the formation of volatile ammonium sulphate.

(2) Considers sodium as the only base whereas potassium ammonia, etc., might be used and would throw out the calculation.

(3) Ash is apt to contain sodium salts, *i. e.*, sulphide, oxide and chloride.

(4) There is a possibility of barium salts of sulphonic acids being insoluble in water.

(5) The barium chloride method for precipitating sulphates especially in the cold, has apparently given trouble to some of the Committee who have tried it.

Suggested improvements, mostly by Dr. Hill himself:

(1) In view of possibility of some sulphate being reduced to sulphide by organic matter, treat ignited barium sulphate with small amount of sulphuric acid and re-ignite.

(2) As some barium salts of sulphonic acids are difficultly soluble, use larger quantities of hot water to wash precipitate.

(3) Chlorides must be separately determined, calculated to Na_2SO_4 and deducted from the weight of ignited residue.

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(4) Ammonia must be separately determined, calculated to Na_2SO_4 and added to the weight of ignited residue.

(5) If potassium is present, the ignited residue should be dissolved in water, analyzed for sulphate and the result calculated to Na_2SO_4 this value being used in place of weight of ignited residue.

Englund's Method

Criticisms chiefly by Dr. Hill.

(1) The decomposition of sulphonic acids by boiling with hydrochloric acid, while taking place readily with some sulphonic acids practically does not take place at all with others, such as napthalene sulphonic acid. Assuming that the decomposition was complete however, this determination will actually give the acidity corresponding to the sulphuric acid plus twice the sulphonic acid plus the sulphonic acid corresponding to its sodium salt. The sulphuric acid is of course unchanged and will show up as is. The sulphonic acid would be hydrolyzed and would therefore show twice its normal acidity while the combined sulphonic acid would be liberated from this salt and hydrolze giving an apparent acidity corresponding to its salt. A condensed sulphonic acid which may contain only one sulphonic acid group may contain a number of SO_2 groups in the R group. This R group would probably be broken up and show all the SO_2 groups as sulphuric or sulphonic acids.

(2) Some calcium sulphonates are apt to be insoluble. Thorough washing of the precipitate to wash out any difficultly soluble sulphonates will wash through considerable quantities of calcium sulphate which is quite appreciably soluble in hot water. Oxidation of sulphonates may be a very difficult operation and again as in Method 1, the R group may break up giving very high results.

Method 3 assumes all other parts of the synthetic tannin soluble in ethyl alcohol except neutral sulphates.

Hayes' Method

Parts B and C are open to same criticisms as Dr. Hill's method with the additional criticisms of Part C that sulphuric acid is only driven off by strong ignition.

Experimental results of the above methods are shown in the accompanying tables.

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Additional Experimental Results

Dr. Hill reports the following:

Englund's Method, Part1:

Gives only the acidity, and no hydrolysis takes place. As a basis for this statement, he gives the following results.

	Sample No. 1 Per cent acid	Sample No. 3 Per cent acid
(1) No hydrochloric acid	11.20	5.12
(2) 10 cc. of normal hydrochloric acid (no heating)	11.20	5.12
(3) 10 cc. of normal hydrochloric acid ½ hour's boiling	11.20	5.12
(4) 10 cc. of normal hydrochloric acid (2 hours' boiling)	11.20	5.12

Hayes' Method, Part C:

By carrying on experiments in an electrically heated muffle, on different days, at as nearly as possible the same temperature, he came to the conclusion that while determinations made under exactly the same conditions check each other very well even when the time of heating is varied, determinations carried out at slightly different heats do not check at all. The indication is that the discrepancy is due to the different extent in which sulphuric acid is removed under varying conditions. Since the method does not completely remove the free sulphuric acid from the sulphates it appears to be worthless.

Hill's Method, Part 2:

The time of standing before filtering does not effect the results:

Time of standing	Sample No. 2	Sample No. 3
3 hours	3.81	4.18
3 "	3.99	4.28
6 "	3.85	4.20
6 "	3.85	4.27
24 "	3.85	4.07
24 "	3.87	4.09
72 "	(3.46)	3.88
72 "	3.80	4.18
Average	3.88	4.14

Klipstein reports the following:

Englund's Method, Part 1:

Is very unreliable as with any increase in the amount of hydrochloric acid used for hydrolysis, there is a steady increase

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in the percentage of sulphuric acid found in the sample regardless of the number of hours (from 1 to 17) boiled under a reflux condenser. This can be readily seen from the following tables:

Sample No 1.

Weight Gm.	HCl acid Cc.	Hours boiled under reflux	H_2SO_4 found Per cent
1.0	25 N/2	1	11
0.680	25 N/1	17	23
0.563	25 N/1	17	26.9
.0.425	25 N/1	17	33.8
0.347	25 N/1	1	44.4
0.174	25 N/1	17	60.5

Sample No. 2.

Weight Gm.	HCl acid Cc.	Hours boiled under reflux	H_2SO_4 found Per cent
1.0	25 N/2	1	2.25
0.235	25 N/2	1	2.92
0.2	50 N/2	1	8.5
0.417	25 N/1	17	20.15
0.347	25 N/1	1	27.5
0.19	25 N/1	17	46

SYNOPSIS OF THE EXPERIMENTAL NOTES OF VARIOUS MEMBERS

Hill's Method:

(1) Spits badly on ashing even after drying over night as a regular ash.

(2) Ash contains considerable impurities from its appearance, and would probably necessitate a sulphate determination.

(3) In samples 2 and 3 the H_2SO_4 calculated from the ash is decidedly higher than from the determination of total H_2SO_4. Therefore more alkali has been added than sufficient to neutralize all the sulphuric acid present. Some of the sulphonic acids have been neutralized. Alkali used to neutralize sulphonic acids appears in the ash.

(4) Difficulty was experienced in retaining the barium sulphate precipitate on the filter.

(5) Barium sulphate precipitate could not be washed white with dilute HCl indicating the presence of insoluble organic compounds. The precipitate whitened on heating but gave compounds soluble in hydrochloric acid which gave a precipitate with sulphuric acid indicating probable reduction of insoluble compounds to soluble ones. This would appear to give erratic results for total sulphates, low if $BaSO_4$ was reduced to sulphide, and high if insoluble barium sulphonates were left on the filter.

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Englund's Method:

(1) The color of the solution masks the color change of an indicator. Dilute hydrochloric acid does not break up sulphonic acids, or if it does the action is not complete. Found that titration was sharper and easier to read by diluting (after refluxing) to a large volume. Sample 3 gave a very difficult end point.

(2) A large quantity of water is required to wash out excess lime. This water will dissolve out the calcium sulphate. 0.214 gram calcium sulphate dissolve in 100 cc. water at 40° C. (Treadwell and Hall, **1**, page 111). Insoluble organic compounds are formed. Filtrate contains large amounts of calcium. On adding oxidizing agents before adding barium chloride solution, a heavy precipitate presumably of calcium salts came down. On the other hand barium chloride solution will give a precipitate with the filtrate before adding oxidizing agents. Oxidizing with nitric acid, a precipitate will come down after repeated filterings even after a week's standing in a warm place. This shows that oxidation is very difficult and complete oxidation is nearly impossible. The addition of lime renders the syntans alkaline and hence will precipitate insoluble compounds of a "Bakelite" nature.

(3) Filtration with alcohol was very troublesome for Nos. 2 and 3, in fact, almost impossible for No. 3. Alcohol insoluble residues from Nos. 2 and 3 were dark and gummy and did not look like inorganic sulphates.

Hayes' Method:

(A) Procter and Searle acid determination gives very erratic results. Great care has to be taken to avoid spitting. Duplicate results do not check at all. Difficulty was experienced in carbonizing the residues after evaporation to a point when resultant leached solution could be titrated.

(B) Same as second part of Dr. Hill's method.

(C) Same as in first part of Dr. Hill's method. Results are too high.

Conclusion of Members

Blackadder: Considers Hill's method unsuitable, and that a method on some other basic principle is necessary.

J. S. Downing: Difficulty with barium chloride precipitation.

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G. V. DOWNING: Had experimental difficulties with barium chloride precipitation.

FREY and CLARKE: Consider all the methods very unsatisfactory, involving too many doubtful theoretical considerations and side reactions.

ENGLUND: Considers his own method absolutely unsatisfactory.

HILL: The results of the three proposed methods do not show favorably for a determination of free sulphuric acid by any one of the methods. The determination of total soda and total sulphates are fairly simple, and show whether sufficient alkali is present to neutralize the sulphuric acid.

KERNAHAN: Does not think any of these methods will work —all lack quickness and accuracy.

KLIPSTEIN: Considers all methods very unsatisfactory.

KOHN: Did not do experimental work as has been opposed to the sulphuric and sulphonic acid determination from the beginning. States that it is practically impossible to determine sulphuric acid and sulphonic acids in a mixture of these and their salts. They would be in equilibrium and this equilibrium would be seriously effected by temperature and concentration and by the removal of one of the components. Even if sulphuric and sulphonic acids could be distinguished, all sulphonic acids have not tanning properties and some of them are almost as injurious as sulphuric acid. Therefore useless to distinguish between them. Must distinguish between sulphonic acids with tanning properties; and all other acids including sulphonic acids, with no tanning properties.

SMOOT: Considers all methods very unsatisfactory, and offers a method which combines the good points of all the methods.

KRAFT: Unable to finish his work.

HAYES: Worked out another method considering his first method unsatisfactory.

SUBSEQUENT IDEAS SUGGESTED

Smoot submitted a method based on his observations of the failings of Hill's, Englund's, and Hayes' methods. It is really a modification of Hill's method, suggesting the oxidation of the

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barium sulphate filtrate. He also includes Part 3 of Englund's method.

Frey and Clarke submitted a method based on Part 3 and 3b of Englund's method; Hill's barium sulphate precipitation; and oxidation of the original extract with nitric acid and Eschka's mixture. They suggest the possibility of washing precipitates with some organic solvent to wash out organic impurities.

Klipstein suggests the use of a similar method to that used in determining the sulphuric acid in leather. Evaporate the extract slowly, re-dissolve in alcohol, filter, titrate, filtrate for acid content.

Hayes submits the following method and results:

PROCEDURE

Weigh 2-2½ grams of the syntan into a 200 cc. graduated flask, add 100 cc. of a solution containing 1 per cent gelatine (neutralized) and 1 per cent sodium chloride, make up to volume and shake. Let it stand overnight in the cold. Filter, using kaolin but no digestion is necessary.

Titrate 25 cc. of the clear filtered solution against any N/10 alkali, preferably barium hydroxide, using methyl orange as indicator. This titration figure represents the total free strong acid and determines the amount of barium hydroxide to be added for the precipitation of the free sulphuric acid. Continue the titration using phenolphthalein or preferably add an excess of alkali and titrate back, using phenolphthalein as indicator. Any increased acidity would represent the weak acids.

Dilute 50 cc. of the clear, filtered solution to 400 cc., add 12 cc. concentrated HCl, heat to boiling, and add the calculated amount of N/10 barium hydroxide as determined by the previous titration. Digest on the steam bath for four hours with occasional stirring. Filter rapidly by decantation. It is desirable to separate the precipitate from the liquid while the solution is near the boiling point to insure solution of the barium sulphonate. Wash the precipitate thoroughly with hot dilute HCl and then with hot water. Ignite the precipitate and if necessary moisten it with a drop or two of sulphuric acid, and re-ignite. Calculate the barium sulphate to free sulphuric acid.

We have made the following determinations:

A — The total free acidity by the back titration method.
B — The free, strong acidity by direct titration.
C — The free sulphuric acid by the precipitation method.

My assumptions are that:

B — C = the free sulphonic acid.
A — B = weaker acids not sensitive to methyl orange.

Tabulation of results obtained on the four samples of syntans submitted using the above method per one gram of syntan.

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	I	II	III	IV
Sulphonic Acid				
Cc. N/10 free acid	15.97	.83	4.83	7.68
Weaker Acids				
Cc. N/10 free acid	.72	1.28	3.48	1.29
Free Sulphuric Acid				
Per cent free acid	.67	.09	.09	1.38
Cc. N/10 " "	1.36	.18	.16	2.83

Dr. Kohn's method for determining the correct acidity in syntans was submitted to the Committee for criticism. At the same time their attention was drawn to Dr. Kohn's article in the April, 1922, number of the J. A. L. C. A. While up to date only about half of the Committee have replied, the general opinion seems to be that this is a very practical way of solving a difficult problem.

The following is Dr. Kohn's method as submitted:

DETERMINATION OF CORRECT ACIDITY IN SYNTANS

Take such an amount of syntan as represents 0.4-0.5 gram actual tan, dilute to 100-200 cc. and shake with 5-6 grams of air dry hide powder for 10 to 30 minutes.

A little of the solution is then filtered and tested for tan and acidity.

A. If the solution is acid to methyl orange and free from tan (Gelatine test) the acidity is too high.

B. If the solution is neutral, or very slightly acid, and shows tan after acidifying. The acidity of the original is too low.

C. If the solution is acid and also shows tan, it must be shaken longer or a little more hide powder used (but it is important to avoid excessive amounts of hide powder).

The correct acidity is indicated when the solution is neutral or very faintly acid and shows no tan or only a very faint test for tan on acidifying.

The great variety in composition and nature of syntans makes it impossible to define details of procedure (concentration, proportions, time of shaking, etc.) which will fit all preparations. These details of procedure will vary and have to be determined for each class of syntans separately by a very careful study of the influences of the various constituents of the product.

A few tests were run in the chairman's laboratory on Dr. Kohn's method. It seemed to be very simple and easy to manipulate. The following results were obtained.

	Dilution	Amount of hide powder Grs.	Acidity
Sample No. 1	2.5 cc. 100	6	Considerable excess
Sample No. 2	2.5 cc. 100	6	Slightly insufficient
Sample No. 3	2.5 cc. 100	6	Slightly insufficient
Sample No. 4	2.5 cc. 100	7	Correct

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HILL'S METHOD—ALL RESULTS CALCULATED TO H_2SO_4—AVERAGE RESULTS ONLY

Experimentor	Sample No. 1			Sample No. 2		
	1 Ash Na_2SO_4 calculated to H_2SO_4	2 Total H_2SO_4 and sulphates	3 2 − 1 free H_2SO_4	1 Ash Na_2SO_4 calculated to H^2SO_4	2 Total H_2SO_4 and sulphates	3 2 − 1 free H_2SO_4 (a)
G. V. Downing	.224	4.305	4.081	8.25	5.375	—2.875
Hill	.14	2.46	2.32	8.03	3.90	—4.13
Frey	.233	2.755	2.522	8.74	3.89	—4.85
Clarke	.115	2.78	2.665	8.31	3.74	—4.57
Blackadder	.185	3.73	3.545	8.42	4.88	—3.54
Faust and Glass	.194	3.89	3.696	8.75	4.39	—4.36
Kraft		3.90			5.22	
Kernahan	.17	0.52	0.35	8.67	5.43	—3.24
Smoot	.33	3.90	3.57	8.34	4.80	—3.54
J. S. Downing	.25	2.99	2.74	8.57	4.52	—4.05

Note:—(—) or negative results for free sulphuric acid are shown on samples 2, 3 and 4 for comparative purposes only. Thus —2.76. would indicate that sufficient alkali has been added to neutralize not only all the sulphuric acid present but to neutralize 2.76% more if it were present. This excess alkali presumably neutralizes part of the sulphonic acid present.

HILL'S METHOD—ALL RESULTS CALCULATED TO H_2SO_4—AVERAGE RESULTS ONLY.

Experimentor	Sample No. 3			Sample No. 4		
	1 Ash Na_2SO_4 calculated to H_2SO_4	2 Total H_2SO_4 and sulphates	3 2 − 1 free H_2SO_4 (a)	1 Ash Na_2SO_4 calculated to H_2SO_4	2 Total H_2SO_4 and sulphates	3 2 − 1 free H_2SO_4 (a)
G. V. Downing	10.61	6.55	—4.06	3.39	4.27	.88
Hill	9.93	4.08	—5.85	3.24	2.40	—.84
Frey	10.38	5.18	—5.20	3.42	3.24	—.18
Clarke	10.76	4.74	—6.02	3.29	3.11	—.18
Blackadder	10.645	5.710	—4.935	3.40	3.84	.44
Faust and Glass	9.90	4.46	—5.44	3.14	3.65	.51
Kraft		5.61			4.02	
Kernahan	10.53	8.92	—1.61	3.37	1.23	—2.14
Smoot	10.68	5.60	—5.08	3.07	3.71	.64
J. S Downing	10.65	5.25	—5.40	3.90	3.56	—.34

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HAYES' METHOD—ALL RESULTS CALCULATED TO H_2SO_4.

Experimentor	Sample No. 1 A Free H_2SO_4 and free sulphonic	B Free H_2SO_4 sulphates	C Sulphates	B-C Sulphuric H_2SO_4	A-B & C Sulphonic	Acidity by titration	Sample No. 2 A Free H_2SO_4 and free sulphonic	B Free H_2SO_4 sulphates	C Sulphates	B-C Sulphuric H_2SO_4	A-B & C Sulphonic	Acidity by titration
Frey	20.39	2.84	0.012	2.83	17.56		6.08	3.94	4.21	—0.27	6.35	
	19.65	2.67					15.88	3.84		—0.37	16.25	
Clarke	13.31	2.78					4.19	3.74				
Englund						9.48						
G. V. Downing		4.305				11.5		5.37				2.9
Hill		2.46	0.09	2.35		11.55		3.90	4.74	—0.84		2.61
									6.70	—2.80		
Faust and Glass	18.22	3.65				11.15	0.1	4.39				2.69
Kernahan	12.02	0.52	0.06	0.46	11.56		6.08	5.43	6.70	—1.27	7.35	
Smoot	2.22	3.90		3.90	1.68		1.63	4.80	6.07	—1.27	2.90	

HAYES' METHOD—ALL RESULTS CALCULATED TO H_2SO_4.

Experimentor	Sample No. 3 A Free H_2SO_4 and free sulphonic	B Free H_2SO_4 sulphates	C Sulphates	B-C Sulphuric H_2SO_4	A-B & C Sulphonic	Acidity by titration	Sample No. 4 A Free H_2SO_4 and free sulphonic	B Free H_2SO_4 sulphates	C Sulphates	B-C Sulphuric H_2SO_4	A-B & C Sulphonic	Acidity by titration
Frey	12.20	5.20	10.03	—4.83	17.03		13.05	3.43	2.55	0.88	12.17	
	11.74	5.17					12.75	3.06				
Clarke	5.72	4.74					6.83	3.11				
Englund												
G. V. Downing		6.55				5.8		4.27				7.6
Hill		4.08	3.40	—0.68		5.03		2.40	2.26	0.14		7.15
			8.05	—3.97					2.23	0.17		
Faust and Glass	4.51					7.60	5.59	3.65				6.86
Kernahan	12.29	8.92	10.09	—1.17	13.46		11.06	1.23	2.94	—1.71	12.77	
Smoot		5.60	5.85	—0.25			0.70	3.71	2.29	1.42	—0.72	

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ENGLUND'S METHOD—ALL RESULTS CALCULATED TO SULPHURIC ACID H_2SO_4.

Experimentor	1 Sulphuric sulphonic acids and sulphonates	Sample No. 1 2A Sulphonic acid and sulphonates	Sample No. 1 2B Sulphuric acid sulphates	3 Sulphates	1-2A Sulphuric acid	2B-3 Sulphuric acid	3B Sulphuric sulphonic sulphonates
Hill	11.20	5.10 to 7.66	nil	Trace	3.54 to 6.10	nil	
Frey	11.60	18.48	0.027	0.00	6.88	0.027	19.30
Clarke	11.50		0.453	0.00	3.97	0.453	8.90
	11.53	7.56	0.00			0.00	
Faust and Glass	11.27	10.55	1.40	trace	0.72	1.40	
Englund	11.23	3.40	0.20		7.83		
Klipstein	11.0 to 60.5	4.38	4.47	1.89	6.62 to 56.12	2.58	
		Sample No. 2					
Hill					—4.40		
	2.40	6.80	nil	6.17	—6.77	—6.17	
	2.40	to 9.13		5.07	—6.73	—5.07	
Frey	2.74	11.58	0.024	7.05	—8.84	—7.026	5.17
Clarke	2.68	—	4.86	5.40	—4.61	—0.54	2.44
	2.73	7.29	0.94	—	—4.64	—4.56	
Faust and Glass	2.64	2.54	1.715	5.36	0.10	—3.654	
Englund	1.84	5.02	trace		—3.18		
Klipstein	2.25	5.90	5.86	4.20	—3.65	+1.66	
	46.0				to+40.10		

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ENGLUND'S METHOD—ALL RESULTS CALCULATED TO SULPHURIC ACID H_2SO_4.

Experimentor	1 Sulphuric sulphonic acids and sulphonates	Sample No. 3 2A Sulphonic acid and sulphonates	Sample No. 3 2B Sulphuric acid sulphates	3 Sulphates	1-2A Sulphuric acid	2B-3 Sulphuric acid	3B Sulphuric sulphonic sulphonate
Hill	5.12	4.90	nil	9.17	0.22	—9.17	
	5.12	7.—6		9.60	—1.94	—9.60	
Frey			.012	—		—6.728	16.96
		25.10	.061	6.74		—6.679	18.36
Clarke		9.01	.343	8.02		—7.677	16.10
Faust and Glass	7.84	13 55	nil	6.02	—5.71	—6.02	
Englund	4.70	6.15	trace		—1.45		
		Sample No. 4					
Hill	6.57	5.17	nil	2.04	+1.40	—2.04	
	6.57	6.00		2.51	+0.57	—2.51	
Frey	7.04	17.42	0.73	2.44	—7.38	—2 367	15.12
Clarke	7.20	15 53	0.82	2.18	—8.33		14.80
	7.15	7.93	0.00		—0.78		
Faust and Glass	6.90	6.55	0.00	7.86	+0.35	—7.86	
Englund	7.07	3.53	slight trace	—	3.54		

3B as worked by Clarke and Frey consists in boiling down the alcoholic filtrate from 3 to dryness oxidizing the residue and estimating the sulphates in it.

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Summary of Report

1. No quick practical method is apparent for the determination of sulphuric and sulphonic acids in synthetic tanning materials.

2. That it is very doubtful if it would be of any practical use if these acids could be separately determined.

3. That Dr. Hill's method is the most promising in approximating the amount of free sulphuric acid present.

4. That Dr. Kohn's methods, or some modification of them. promise to show whether syntans contain an excess of any harmful acidity.

Additional Information

Many proposed methods were submitted for the formaldehyde determination but due to complications arising from the acid determination it was decided to concentrate on the latter points until it was settled. Dr. Kohn's method as submitted and explained in his paper, appears to offer a solution of the adaptation of the official method.

The question of ash determination is covered by Dr. Hill's method, part 1 or by the official method.

The following preliminary examination by Dr. Hill is of interest.

	No. 1	No. 2	No. 3	No. 4
Per cent water	73.50	26.5	46.0	19.5
Color 10 per cent solution	C 7	C 11½	C 3	C 7
Acidity as H_2SO_4	11.55	2.61	5.03	7.15
Sp. Gr. at 25° C.	1.163	1.157	1.280	1.163
Solution	Clear	Clear	Clear	Clear
Chlorides	None	None	None	None
NH_3	None	None	None	.018%
K	None	None	None	None

The following results were obtained in this Chairman's laboratory and appear of interest.

Analysis by Official Method

	No. 1	No. 2	No. 3	No. 4
Twaddell @ 60° F.	32¼	31¾	62¾	33
Tannin	33.45	10.03	29.91	19.65
Non-Tannin	5.46	15.34	27.84	13.50
Insolubles	0.00	0.00	0.00	0.00
Water	61.09	74.63	42.25	66.85
Total solids	38.91	25.37	57.75	33.15
Soluble solids	38.91	25.37	57.75	33.15

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Ash	0.28	12.65	14.35	4.55
Acidity on non-tannin filtrate calculated to per cent H_2SO_4 on original syntan	1.96	1.31	2.94	1.63
Acidity of original extract calculated to H_2SO_4	11.15%	2.69	7.60	6.86

PLUMPING VALUE BY CLAFLIN'S METHOD

PROCEDURE.

Solution made up 5 cc. syntan in 200 water, add 5 grams of dry hide powder. Shake well in shaker for ten minutes. Allow to stand 24 hours. Filter through cloth without squeezing. Allow to completely drain and measure volume of filtrate. All syntans dissolved in cold water. No. 5 is liquid sulphited quebracho dissolved in hot water and rapidly cooled at 66° F.

Extract No.	Volume of filtrate cc.	Liquid absorbed cc.	Filtrate
1	142	58	Turbid
2	145	55	Clear
3	142	58	Clear
4	120	80	Slightly turbid
5	126	74	Very turbid

Some work was done on the penetrating value on gelatine gels of solutions of various strengths. It was found difficult to distinguish between penetration and solution. If the solution was too strong and the gelatine too weak a dissolving action occurred and not a penetration.

The bleaching action was tried on quebracho tanned sheep skin skivers and on the tanned hide powder from a solid quebracho non-tannin estimation. The bleaching effect could be seen by comparing with the original.

STUDIES OF THE STRENGTH OF PROTEOLYTIC ENZYMES IN THE PROCESS OF BATING*

By Charles S. Hollander

Commercial enzyme bates have for a number of years replaced the dung bates in almost every instance, and through this extended period of time it has been ascertained that the artificial

* Read before the Leather Section of the A. C. S. in Pittsburgh, Sept. 6, 1922. Published by courtesy of the American Chemical Society.

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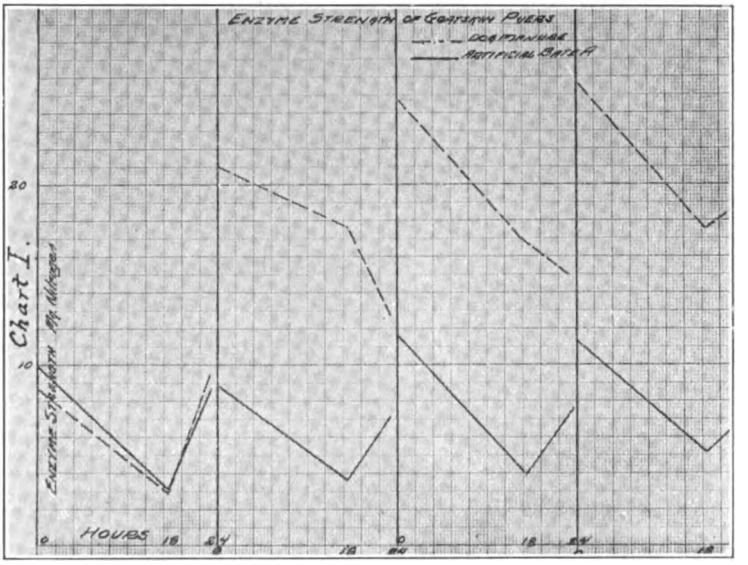
bates, properly used, give as good finished leather as ever was manufactured by the old process.

In a paper recently read at the Convention of the American Leather Chemists' Association,[1] some histological aspects of the process of bating were pointed out. With the aid of some very interesting photomicrographs it was shown that the function of a bate or puer, aside from deliming, was not so much a dissolving action, but at most the fragmenting and loosening up of the elastin fibers. The view was put forward, based on a general consideration of the whole bating process, that one of the functions of a bate far more important than the incidental action on the elastin fibers, was the digestive action on the so-called inter fibrillary substance.

In conjunction with the bating experiments already described there in full detail, an examination of the strength of the enzyme



in the bate liquors was systematically undertaken which may help to throw some further light on the chemical processes involved in the processes of bating.

[1] A. L. C. A., 17, 542, 1922.

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In *Chart I* is represented the graphical comparison of an artificial bate and a dog manure bate, as used for manufacture of goatskins. The curves, representing the strength of the pancreatic enzymes in the artificial bate are represented by a solid line. The enzyme strength, as expressed in milligrams of nitrogen,[2] is very uniform and shows a tendency of dropping in strength over night to a minimum value. After the removal of the skins after about sixteen hours, the liquor was kept until used in the afternoon of the same day for a preliminary puer for the next batch, and, during that interval, the enzyme strength again is in part recovered. I venture to say that this movement of the curve is explainable by assuming that the original enzyme present gradually disappears and that proteolytic enzymes of bacterial origin replace it. These develop during the period of "rest" between the sixteenth and twenty--third hour to such an extent that the enzyme strength is in part recovered.

The broken line represents the strength of the enzyme as found in the old time dog manure puer. The parallelism for the first twenty-four hours is quite remarkable, but after that the dog manure commences to act in an entirely different way. As you know, there is no preformed enzyme in the dog dung discoverable by the usual methods. Enzymes develop only after the fermentation of an infusion and are entirely of a bacterial origin; consequently we must not be surprised at the more or less irregular and uncontrollable behavior. You see on the second day that the strength of the enzyme, into which the fresh skins were introduced, is more than twice as much as on the first day. On the third day and fourth day, the enzyme strength is fully three times as much as on the first day. On the other hand, the recovery of any strength is irregular. On the first and fourth days, the strength was recovered to some extent, while on the two intermediate days the strength consistently dropped during the period of rest.

Chart II shows you a graphic comparison of the strengths of dog manure and another grade of artificial bate, which is different from the first only in the nature of the delimer used. Al-

[2] In each case 10 cc. of the puer or bate was taken for the strength determination made according to the total nitrogen method described by Sherman and Neun, *J. A. C. S.*, 38, 2203, 1916, for one hour at 40° C.

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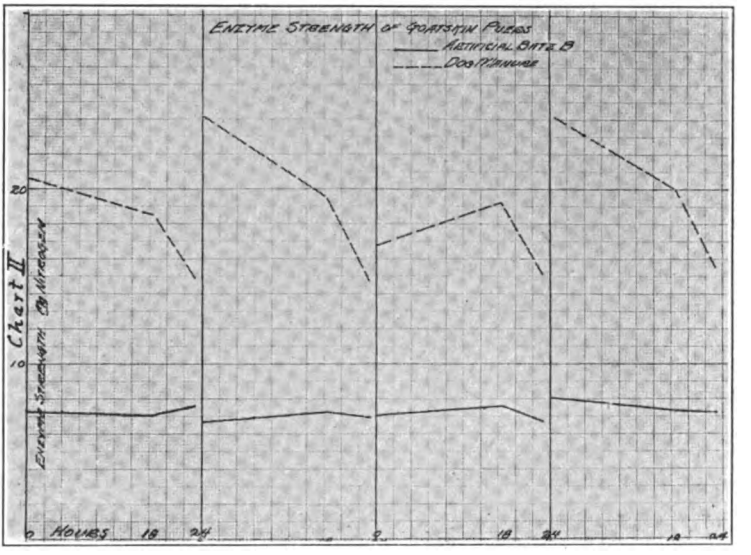

though the same concentration of dog manure was used, you see in this second chart that the initial strength is more in keeping with the higher ones of the previous chart, and show consistently a decline in enzymes, due no doubt to the decomposition of the proteolytic enzymes generated by the bacteria and lack of propagation of fresh bacteria. On the other hand, the strength of the artificial puer is quite uniform and varies so little that the small changes are within the limits of accuracy of the enzyme determination.

The *third chart* shows us another comparison with dog manure and a third grade of artificial bate, suitable for puering goatskins, with a third type of delimer. Again we see that the artificial bate in its action is quite uniform while the curve of the dog manure strength shows great irregularities, especially compared with previous charts. Even a casual examination of these charts will show you how extremely difficult it was in the old days of manure bating to get uniform results, and in fact the beamster was on the lookout for unexpected happenings at almost any time. It was his usual routine to visit his puer vats at about 8 o'clock at night and then again at 11 o'clock to see how the fermentation was proceeding. His experience had taught him that, if the fer-

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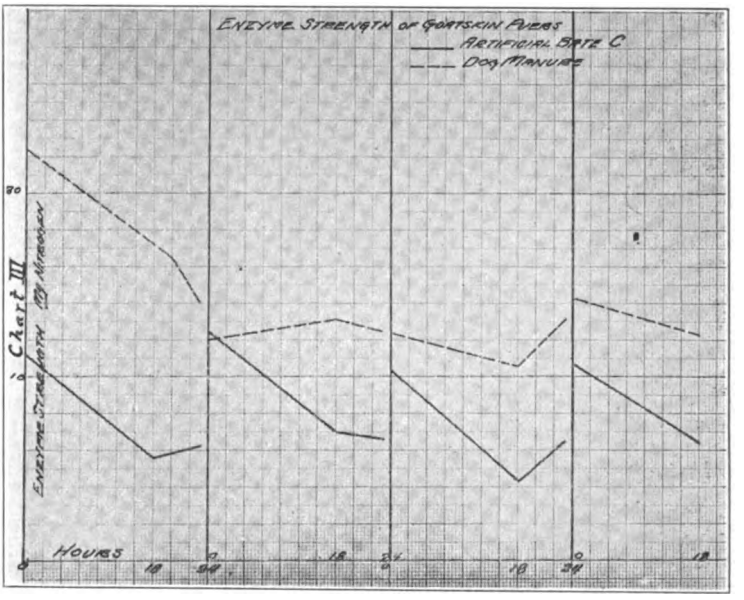

mentation by 11 o'clock was getting too wild, the temperature had to be reduced in order to prevent the skins from "falling." This "falling" is quite a disastrous thing to happen, and, if the skins are once raised to the surface as they should be and left beyond their time in the puer, they all of a sudden drop down to the bottom of the tank and then they are irretrievably spoiled. No good leather can be made from them any more. If you keep all of these variations of the strength of dog manure in your mind, and also the disastrous results which might be expected if neglected in any way, you can easily understand the trials and tribulations of the old time beamhouse foreman, and it is quite easy to see why the uneventful regularity of the artificial bate has been able to displace the uncertainty of the manure bate in every case.

The next two charts represent bating of an entirely different nature, namely of calf skins. Although the goatskins and the calfskins in this case are manufactured for exactly the same use, *i. e.*, for shoe uppers, they require fundamentally different treatment. Goatskins come from mature animals and are of a

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very hard and flinty nature, while calfskins are taken from quite young animals and are very soft and silky in their texture. It will therefore be easily understood that, while the goatskins require a very severe enzyme bating at a high temperature during a long period, the calf skins only undergo a bating with a weaker enzyme during a very short period and at considerably lower temperatures.

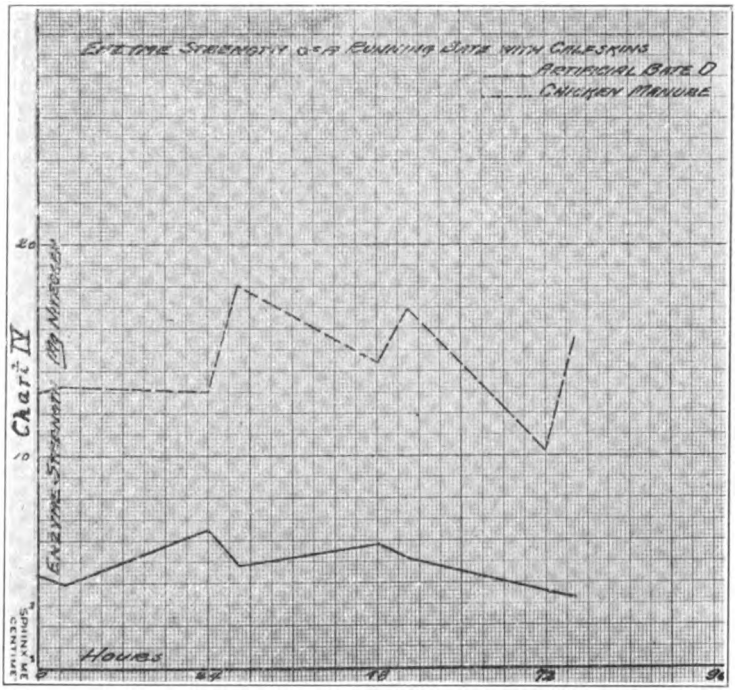

Chart IV shows the graphic comparison of the strength as found. While chicken manure itself does not contain any preformed proteolytic enzymes, we have quite an abundance of them after fermenting but they are all of bacterial origin and the shape of the curve shows that they are quite uncontrollable. Running up on the twenty-four hour line, we see that the artificial bate rises in strength which is entirely due to addition of fresh enzyme, while the strength of the chicken manure bate remains practically the same, although an addition had been made to it. The enzyme

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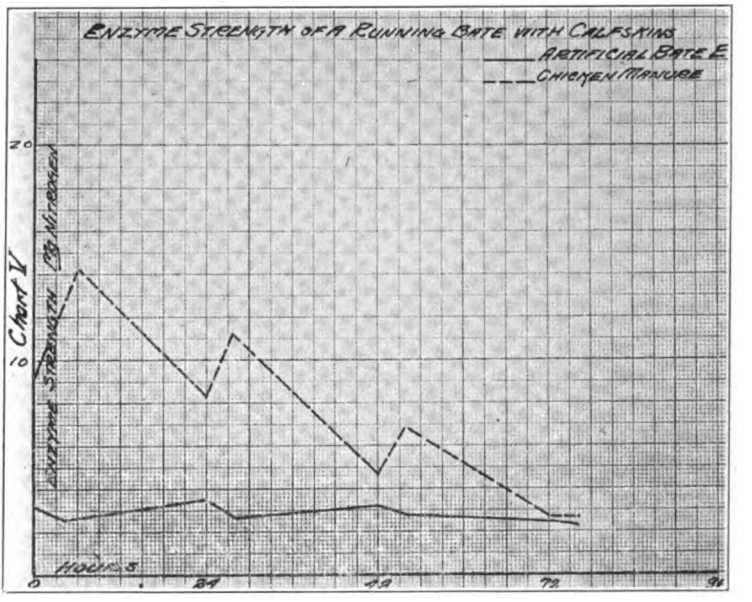
strength changes quite regularly during the bating operation and, as you see, in opposite direction; with the artificial bate, the enzyme strength decreases during the bating operation and increases by addition of fresh bate to keep the strength at approximately the same level, while with the chicken manure bate the enzyme strength increases during the bating operation and decreases during the rest period.



We see exactly the same in *Chart V*. The broken line again represents chicken manure and it is quite as irregular as during the former four-day period, rising in strength toward the end of the bating operation and declining during the rest period, to again rise during the next bating operation, etc., while the artificial bate behaves exactly opposite although here a different deliming agent has been used.

We know for a certainty that the quality of the leather produced with artificial bates, using pancreatic enzymes, is equal in every respect to the leather made by the old time manure process. Therefore the question arises: Why do the enzyme strengths

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of artificial bates and dung bates show such great differences? The conclusion reached is that the pancreatic enzyme must be entirely different from the enzyme liberated by bacteria. In bating under practical conditions the amounts of pancreatic enzymes chosen are equivalent to the amounts of manure bate chosen as measured in terms of manufactured leather, but the enzyme strengths, as compared on other media—in our case casein—are not equivalent. It is therefore misleading and useless to attempt to measure the enzymatic efficiency of any enzyme bate if we use media which are so different from skin substance as casein, gelatin, fibrin, etc. We have always assumed that each enzyme is specific and therefore we should not be surprised to see that, while an enzyme may digest certain constituents of the skin, nevertheless they may not register with the same efficiency in our casein or gelatin methods. The methods, as described in the literature so far, are merely an aid to control the strengths of artificial bates for their manufacture.

TABLE I.

50 MG. PANCREATIN PREPARATION NO. 1, 1 HOUR AT 40° C.

Added Dissolving period*)	Digesting period**)	Mg. N
—	—	14.7
—	2 Gr. NH_4Cl	18.4
—	0.15 Gr. soap	13.6
—	2 Gr. NH_4Cl ± 0.15 gr. soap	14.6
2 Gr. NH_4Cl	—	76.0
2 Gr. NH_4Cl + 0.5 gr. cane sugar	—	76.3
2 Gr. NH_4Cl + 0.5 gr. corn sugar	—	76.5
2 Gr. NH_4Cl + 1.5 cc. CH_2O (40%)	—	48.5
2 Gr. NH_4Cl + 0.5 gr. NaH CO_3	—	83.0
2 Gr. NH_4Cl + 0.15 gr. soap	—	37.3
2 Gr. NH_4Cl	0.5 Gr. cane sugar	76.9
2 Gr. NH_4Cl	0.5 Gr. corn sugar	75.5
2 Gr. NH_4Cl	1.5 Cc. CH_2O (40%)	14.5
2 Gr. NH_4Cl	0.15 Gr. soap	66.5
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 0.5 gr. cane sugar	88.2
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 0.5 gr. corn sugar	84.9
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 1.5 cc. CH_2O (40%)	1.4
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 0.15 gr. soap	88.8
0.1 Gr. $NaHCO_3$	—	47.2
0.1 Gr. $NaHCO_3$	2 Gr. NH_4Cl	51.3
0.1 Gr. $NaHCO_3$	0.15 Gr. soap	39.6
0.1 Gr. $NaHCO_3$	2 Gr. NH_4Cl + 0.15 gr. soap	36.6

*Per gram of enzyme preparation.
**Per 100 cc. of casein solution.

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TABLE II.

10 MG. PANCREATIN PREPARATION NO. 2, 1 HOUR AT 40° C.

Added Dissolving period*)	Digesting period**)	Mg. N
—	—	32.5
—	2 Gr. NH_4Cl	32.7
—	0.15 Gr. soap	34.6
—	2 Gr. NH_4Cl + 0.15 gr. soap	34.0
2 Gr. NH_4Cl	—	91.6
2 Gr. NH_4Cl + 0.5 gr. cane sugar	—	92.5
2 Gr. NH_4Cl + 0.5 gr. corn sugar	—	93.7
2 Gr. NH_4Cl + 1.5 cc. CH_2O (40%)	—	53.1
2 Gr. NH_4Cl + 0.1 gr. $NaHCO_3$	—	113.0
2 Gr. NH_4Cl + 0.15 gr. soap	—	44.7
2 Gr. NH_4Cl	0.5 Gr. cane sugar	92.1
2 Gr. NH_4Cl	0.5 Gr. corn sugar	88.0
2 Gr. NH_4Cl	1.5 Cc. CH_2O (40%)	0
2 Gr. NH_4Cl	0.15 Gr. soap	101.5
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 0.5 gr. cane sugar	93.2
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 0.5 gr. corn sugar	90.4
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 1.5 cc. CH_2O (40%)	10.1
2 Gr. NH_4Cl	2 Gr. NH_4Cl + 0.15 gr. soap	103.0
0.1 Gr. $NaHCO_3$	—	82.4
0.1 Gr. $NaHCO_3$	2 Gr. NH_4Cl	79.2
0.1 Gr. $NaHCO_3$	0.15 Gr. soap	80.4
0.1 Gr. $NaHCO_3$	2 Gr. NH_4Cl + 0.15 gr. soap	79.5

*Per gram of enzyme preparation.
**Per 100 cc. of casein solution.

No one has ever isolated a pure enzyme, if there actually be such a thing. Therefore gravimetric methods for determining enzymes are out of the question and so far all methods published only measure the amount of work done under certain fixed conditions such as time and temperature in certain media. The work done by enzymes may be accelerated or retarded by certain influences as will be roughly indicated in the two tables prepared.

Generally speaking you will see that an enzyme preparation *per se* will give low strengths as registered by the casein method. If, however, certain electrolytes are added, the work done under otherwise the same conditions is greatly increased. I have only investigated two such additions, *viz.*, ammonium chloride and sodium bicarbonate, since they are the only ones that need be considered in bating liquors. However, there are no doubt many more substances of this class that will act as accelerators. If compounds of a colloidal nature are added to the enzymes in *dissolving* them, their work seems to be retarded. I have investigated in this respect only soap, since a certain amount of soap may be in the bating liquors. Sugars, such as corn sugar and

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cane sugar, do not seem to have any influence either one way or the other. If these compounds—either electrolytes or colloids—be added during the *digestion* period of the casein solution, they do not exercise much influence, in fact may have a tendency to increase the strength somewhat. I am therefore of the opinion that the presence of certain compounds will either help or hinder the *dissolving* of the enzyme preparation in water.

I may say in this connection that the wood powder used in the manufacture of practically all artificial bates is without influence on the strength of pancreatic enzyme; in fact this medium is nearly ideal in the rôle of an inert absorbent.

Electrolytes counteract to a certain extent the influence of colloids. Since enzyme preparations are never pure chemical compounds, accidental admixtures may vary according to the method of purification; therefore the same weight of actual enzyme of different preparation will measure different in strength. I therefore wish to caution all workers in this field to be extremely careful in drawing conclusions on enzyme strengths, unless all the compounds accompanying the enzyme preparation are always the same.

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BOOK NOTICES

VAN NOSTRAND'S CHEMICAL ANNUAL. Fifth Issue. Edited by J. C. Olsen. Nine hundred pages, flexible leather binding. Price $4.00. D. Van Nostrand Co., New York.

The fifth issue of this handy work of reference which has proven indispensable to the chemist in all branches of work, has been enlarged considerably and thoroughly revised. A considerable number of compounds have been added to the table of organic and inorganic compounds and only the most reliable constants have been accepted. Molecular and atomic weights have been recalculated in accordance with the latest table of atomic weights.

About forty-six new tables of reliable and general information have been included in this issue among which are included temperature corrections for volumetric analysis, hydrogen and hydroxyl ion concentrations of some acids and bases, reaction equations for volumetric computations, chemical and physical properties of several metals, some new specific gravity, vapor tension and solubility tables, chart for the interconversion of Saybolt, Redwood, Engler and absolute viscosities, and others.

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The most welcome feature of this issue is a complete index and the inclusion of a few pages of cross section paper for personal data is a new feature. The revised and new information together with the new features decidedly add to the value and serviceability of this volume. G. W. S.

COLOUR INDEX. Part I. Society of Dyers and Colourists, Edited by F. M. Rowe.

The preparation of the Colour Index by the Society of Dyers and Colourists of which this is the first part has for its object the production of as accurate and comprehensive a work of reference as possible of all the dyes of known constitution which have received commercial names. In this part of the work one hundred and seven dyes are given consisting of nitroso-, nitro-, and mono-azo dyes. The Schultz number is given in connection with the index number; the commercial name is given and where the dye appears under different names they are all given, together with the name of the manufacturers producing them; the scientific name, components and structural formula; preparation, discoverer and literature; description, properties and mode of application are all given and ample space left for notes. In short, everything that is worth knowing about the colors is given briefly and references to the original sources are included.

This information presented in compact tabular form certainly will be found indispensable to all interested in the subject, whether color manufacturer, color user, or student of color chemistry. The work is being put out in parts in suitable form for binding the whole when completed.

ABSTRACTS

Mangrove Swamps of the Sunderbans Forest Division, A Valuable Source of Tanstuffs. By B. M. DAS, *Jour. of Ind. Industries and Labor*, 1, 482 (1921). The author gives a survey of the general occurrence of mangrove, the species and their tannin content. [See Abst. This JOUR., 16, 512 (1922)], which is followed by a review of the investigation conducted by J. A. Pilgrim on the mangroves of the Sunderbans Forest Division. Pilgrim's investigations are summarized as follows:— I. The most abundant species found in the Sunderbans are (1) *sundri* (*heritiera minor*), (2) *goran* (*ceriops roxburghiana*), (3) *gengwa* (*excaecaria agallocha*) and (4) *keora* (*sonneratia apetala*). II. Good extracts can be made from many, but *sundri* and *goran* are the most common and of immediate commercial interest. III. *Pussur* (*carapa moluccensis*) is a valuable material, all parts of the tree, even the wood, giving good results; its reproduction is recommended as it is not abundant. Extract made from *pussur* wood is expected to produce a tannage similar to quebracho. IV. Large scale tanning experiments with the promising materials are recommended. V. The importance of careful collection and preservation of tanstuffs for tannin content and color has been proved and Pilgrim's method of collection and preservation is urged for adoption which consists of crushing or disintegrating the material and drying in the sun.

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Large scale tanning experiments at the Calcutta Research Tannery have succeeded in producing a good colored sole leather by blending *goran* with suitable proportions of *babul* and myrabolan. Tanning experiments are in progress using the bark of *sundri*. The possibilities of mangrove and mixed mangrove extracts are discussed.

Chrome Leather Analysis, IV. A Modified Method of Determining the Amount of Alkaline Salts in Chrome Leather. By D. WOODROFFE and R. E. GREEN. *J. S. L. T. C.*, **6**, 222 (1922). The leather is ashed so as to render any chromium compounds insoluble in acid. The residue is treated with a few drops of sulphuric acid and the excess driven off. Residue is then extracted with hot water, filtered and the sulphates determined in the filtrate by precipitation with barium chloride in the usual way. (Compare Lea. Chem. Pocket Book, p. 197).

Note on the Lyotrope—Adsorption Theory of Gelatine Swelling. By H. G. BENNETT. *J. S. L. T. C.*, **6**, 223 (1922). A reply to a recent article by Atkin in which the author criticizes the attitude of those designated by him as the "osmotic pressure" school.

A Contribution to the Method of Tannin Analysis. By J. SCHNEIDER, JR., *J. S. L. T. C.*, **6**, 234 (1922). A suggested improvement of the I. A. L. T. C. official method by using weighed amounts of solution instead of pipetting. An example is given.

Committee on Limeyard Control, V. The Analysis of Commercial Sodium Sulphide. By W. R. ATKIN. *J. S. L. T. C.*, **6**, 239 (1922). M/15 Na_2S or N/15 NaSH solution is titrated with N/10 acid to $p^H = 10$ using a comparator. Neutral formaldehyde is then added and the solution titrated with N/10 acid using either thymol phthalein or phenolphthalein as indicator. The second titration is a measure of the sulphide content, 1 cc. N/10 HCl = 0.0056 grm. NaSH or 0.0078 grm. Na_2S. The principle underlying the method is discussed in detail.

Contributions to the Chemistry and Technology of Gelatine and Glue. By R. H. BOGUE. Franklin Inst., **193**, 794; **194**, 75 (1922). A comprehensive general article on gelatin and glue combining the material in articles by the author which have already appeared in various publications. The subject is treated under four headings as follows. I. Introduction, subdivided into Historical Considerations and Comparative Statistics. II. Technological Aspects, subdivided into Manufacturing Operations and Valuation. III. Economical Aspects, subdivided into Glue Room Economy, Applications in the Industrial Arts and Gelatin as a Food. IV. Physico-Chemical Research, subdivided into Special Properties of the Colloid State, the Equilibrium between Surface Tension and Solvation Potential, Constitution and Structure.

Leather and Glue. By D. WOODROFFE. *Annual Reports of the Society of Chemical Industry on the Progress of Applied Chemistry*, **6**, 379 (1921). A review of the literature on these subjects for the year 1921 following the general scheme of the previous annual reports.

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The Determination of Water-Soluble Matter in Vegetable Tanned Leather. By W. J. CHATER and D. WOODROFFE. *J. S. L. T. C.*, **6**, 254 (1922). It is claimed that the official (English) method of determining water-soluble matter in vegetable tanned leathers appears to be in error to the extent of 10-30 per cent and that the release of solubles from leather plotted against time gives curves of the same type for different leathers, all of which appear to follow closely laws of an exponential type.

"Goran" Bark: Optimum Temperature and State of Subdivision for Maximum Extraction. A Criticism. By J. A. PILGRIM. *J. S. L. T. C.*, **6**, 255 (1922). The work published by Dhavale and Das under the above title [See Abst., This JOUR., **17**, 128 (1922)] is claimed not to be entirely reliable and that the unexplained variations are due to separating the ground bark into several sizes by sieving in which event the finest particles are the richest in tannin; and analyzing solutions of variable and much lower concentrations than is required officially.

The Cultivation of Tannin Producing Acacias in the French North African Possession. By JALADE. *Le Cuir*, **11**, 329 (1922). There are about thirty species of tannin producing acacias, all of which originated in Australia. Two of the more important species are: *Acacia pycnantha* or golden wattle; and *Acacia decurrens*, of which there are three varieties, *decurrens*, *mollissima* and *dealbata*, commonly known as black, green and silver wattle respectively. The dried bark of these species usually contains 30-40 per cent of tannin. These acacias have been introduced into California but are not grown there for their tannin. They are grown for tannin in South Africa and in the former German colony in East Africa.

The acacies of North Africa are rich in tannin but have not been commercially exploited. A sample of *Acacia lophanta*, collected in Morocco, was found to contain 18.8 per cent of tannin and 7.6 per cent non-tannin. The tannin was rapidly absorbed by hide and produced a leather resembling, in color, oak bark tanned leather. The analysis of a sample of *Acacia decurrens*, also collected in Morocco, showed 38.7 per cent tannin and 8.3 per cent non-tannin if extracted by the official method. and 42.7 per cent tannin and 11.6 per cent non-tannin if extracted in an autoclave at 120° C. This material was also rapidly taken up by hide and produced a firm leather, the lighter colored leather being produced from the liquor extracted in the autoclave at a higher temperature. Analysis was also made of several acacias grown in the experimental garden at Rabat. The percentage tannin found was as follows (moisture 14-15 per cent): *A. pycnantha* bark 42-44 per cent (glucose 4.1 per cent), *A. decurrens* bark 33.9-34.9 per cent, *A. decurrens* pods 29.6 per cent, *A. saligna* bark 20.4 per cent, *A. saligna* pods 14 per cent, *A. cyanophilla* bark 11.7 per cent, and *A. floribunda* pods 11 per cent. The author concludes that the barks of acacias cultivated in Algeria or Morocco are as rich in tannin as those grown in South Africa and could profitably be exported or

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used by the local tanners. In Morocco, *A. pycnantha* will give a better yield than *decurrens;* the bark of these two species contains some reducing sugar contrary to reports by others. The pods may be of value. I. D. C.

One-Bath Chrome Tanning. By P. CHAMBARD and L. MEUNIER. *Le Cuir,* 11, 304 (1922). The tan liquors used in this work were prepared by diluting under carefully controlled conditions (see *J. S. L. T. C.*, July, 1921, p. 222), a stock solution of chrome alum, prepared cold, containing 28.4 grams of chromic oxide per liter. The acidity was determined by the method of Proctor and McCandlish and chrome by Alden's method. Basicity is expressed by Schorlemmer's method; *i. e.*, as the ratio of basic Cr_2O_3 to total Cr_2O_3. The test pieces were prepared from calf butts which had been carefully delimed with formic acid, washed and stored in saturated salt solution. Pieces containing 10 to 10.5 grams of dry substance were used for each test, after washing 48 hours to remove salt. The tanning was carried out in a mechanical shaker. *A. Basic liquors*: Two hundred and fifty cc. of a chrome alum solution, containing 1.73 grams of chromic oxide and having a basicity of 35.6, were used. The basicity rose at first, was 38.8 in 4 hours, then decreased steadily and was only 29.1 in 384 hours. At first therefore acid is absorbed faster than chromic oxide, while later the reverse is true. This agrees with the work of Stiasny and Grillitch. The ratio of chromic oxide to sulphuric acid, CrO_3/SO_3, absorbed tends to become constant as the time of tanning increases. B. *Normal chromic sulphate liquors.* The basicity, which was 0 at the beginning, rose to 2.8 in 4 hours and to 2.9 in 21 hours, then decreased, reaching 1 in 384 hours. The ratio Cr_2O_3/SO_3 again tends to become constant in time. The absolute amount of acid (SO_3) absorbed was always less in this normal solution than in the basic, regardless of time. Saturation or maximum absorption was only reached after 200 hours, not after 24 hours as Grillitch has stated. C. *The progress of tanning in case the bath is renewed.*

Basicity of the tan liquor	Grams of chromic oxide in the liquor	Volume of the liquor	Number of changes of liquor	Time required to reach equilibrium	Chromic oxide absorbed of dry hide substance
35	2.28	119	4	96 hours	10.4
35	1.14	119	4		10.1
35	0.50	250	8	38 days	10.4
17	1.75	100	6	36 days	9.09
17	1.10	250	6	36 days	9.04
0	2.31	100	6	36 days	4.72
0	1.76	250	3	17 days	4.25
0	0.58	250	7	28 days	3.40

For a given basicity, the weight of chromic oxide fixed by hide is, after equilibrium is reached, independent of the concentration of the liquor. If the basicity is zero, the weight of chromic oxide fixed decreases as the concentration decreases. I. D. C.

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Some Notes on Synthetic Tannins. By U. J. THUAU and A. T. HOUGH. *Le Cuir*, **11**, 310 (1922). The work of Hill and Merryman (This JOUR., **16**, 484) is briefly reviewed. The authors believe that Moeller's peptization theory holds for most tanning materials; that is, that these materials are composed of a peptizer, which need to be present only in small amount, and another material which is peptized or made to "dissolve" to a colloidal solution by the peptizer. This latter material is depeptized by the hide and therefore deposited on it. Syntans contain both materials but in mixtures with other tannins act principally as peptizers. As peptizers, syntans have three functions; they dissolve insoluble material or prevent its formation during storage, they change part of the non-tannins, especially phlobaphenes, to tannin and they combine with the tannin of the extract to form more complex tannins and thus brighten the color. I. D. C.

Analytical Recognition of Individual Tanning Materials and of Extracts. Investigation of Mixtures Containing Adulterants. (Plan of work for the Study of these two Questions). By M. JAMET. *Industries du Cuir*, p. 236 (August 20, 1922). Tannins may be separated into the pyrogallol and catechol classes by the following reactions: the reaction with bromine water, ammonium sulphide, acetic acid-lead acetate, formaldehyde-hydrochloric acid and the coloration with Mulhouse bands. Individual tannins may be identified by means of the following reagents: iron alum, nitrous acid, copper sulphate and ammonia, stannous and hydrochloric acids, lime water, lead acetate followed by an excess of soda, and the pine shaving test. The following quantitative tests may also be used; the solubility in ethyl acetate, the molybdenum number, and the determination of pentosans. The solubility of mangrove in ethyl acetate varies from 1 to 5 and of quebracho from 70 to 80. The molybdenum number of mangrove is high and of quebracho low; the number varying from 1 to 135 for catechol and from 80 to 220 for pyrogallol tannins. Quebracho gives a greenish-black precipitate of furfural phloroglucid while mangrove gives the brownish red methyl furfural phloroglucid. These phloroglucides may be determined separately after weighing, by washing the crucible with warm 95 per cent alcohol, in which the methyl compound is soluble, then reweighing. As little as 10 per cent of mangrove may be detected in a mixture with quebracho by this method. Oak bark and chestnut may usually be distinguished by Stiasny's test, or by the fact that for chestnut the ratio of tannin to non-tannin is high and the ash low. However Jedlicka found that the tests were reversed for certain oaks and chestnuts from Slavonia. Tizerah gives all of the reactions which quebracho gives. These materials and also Gonakie pods will be studied further. The study of Mulhouse bands seems promising, trying new mordants, such as the acetates or chlorides of calcium, antimony, uranium, vanadium, titanium or thorium. Also extracts, or residues from extraction with organic solvents, such as ether, amyl acetate or chloroform, might be used as well as aqueous solutions.

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Investigation of Mixtures. The reactions given above may also be used to detect certain extracts in mixtures. The reactions of Procter-Hirsch, Appelius Schmidt or Stiasny may be used for the detection of sulphite cellulose while syntans may be detected by the oxyazo, indophenol or barium chloride reactions. Mangrove in quebracho extract may readily be detected by Schell's cobaltic reaction, the molybdenum number or by the determination of pentosans. Myrobalans in quebracho extract is usually tested for by the acetic acid-lead acetate test but this reaction is indefinite if the amount of myrobalans is low. In this case it is best to remove the quebracho by treating the extract with formaldehyde and hydrochloric acid, filtering and neutralizing the acid by adding sodium acetate before treating with lead acetate. The detection of myrobalans in chestnut extract is difficult, the only methods being a combination of the formaldehyde-hydrochloric acid test, the lead acetate test and the molybdenum number. Tizerah can not be detected in other extracts, except possibly in quebracho, since the ratio of tannin to non-tannin is usually higher for tizerah than for quebracho. There is no satisfactory method for detecting oak or chestnut extracts in mixtures of these two. The color of the Mulhouse bands in the filtrate from the formaldehyde-hydrochloric acid treatment may prove of value for the investigation of pyrogallol tannins in mixtures with catechol tannins. It is planned to study the reactions of myrobalans, mangrove, and tizerah in mixtures with pyrogallol and with catechol tannins and also the acetic acid-lead acetate reaction. An attempt will be made to dissolve the formaldehyde-hydrochloric acid precipitate by treating it either with sodium sulphite under pressure or with organic solvents, and to study the catechol tannins thus formed. I. D. C.

PATENTS

Tanning. Brit. Pat. 180,758. J. HELL, Wurttemberg, Germany. March 1, 1921. Hides and skins are tanned by means of soluble magnesium salts and soluble carbonic-acid salts of other bases in the presence of water. A mixture of the dry salts may be introduced into a drum containing the wet hides, the moisture being sufficient to dissolve the salts and render them active, or the hides or skins may be drummed successively in separate solutions of the salts. The process may be applied to partly tanned hides, or may be combined with other processes such as tanning or treatment by cellulose sulphite liquors, formaldehyde, chrome, iron, or other mineral tanning-agents, or vegetable tanning-agents, used in admixture or separately.

Tanning. Brit. Pat. 181,067. T. B. CARMICHAEL, Waterloo, near Liverpool, and W. H. OCKLESTON, Kelsall, Cheshire. Feb. 24, 1921. Hides are tanned by a combination process which consists in treating the limed hides after washing either successively or simultaneously with an acidified green chrome liquor and a vegetable tanning-liquor. When the solutions are used simultaneously, the hides may be further treated

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with a vegetable liquor or with a series thereof in increasing strengths. The chrome liquor is prepared by dissolving green chrome salts in water to make a solution of 20° Barkometer, to which is added sufficient acetic acid to render 20 cc. of saturated lime-water necessary to neutralize 10 cc. of the liquor. After treatment in the chrome liquor, the hides are drained and then placed in a vegetable tan liquor of about 80° Barkometer or in a floating drum immersed in a vegetable liquor of 80-90° Barkometer, and finally in a liquor of 150° Barkometer at a temperature of 100-120° F. In the combined bath, equal proportions of the acidified chrome liquor and a vegetable liquor of 30-40° Barkometer are used. According to the Provisional Specification, the chrome liquor is acidified with sodium bisulphite.

Depilating Hides, Etc. Brit. Pat. 182,240. O. RICHTER, Brandenburg, Germany. April 13, 1921. The process set forth in the parent Specification for depilating hides or skins by means of gaseous ammonia in certain concentrations, is improved by defatting the skins prior to or in the early stages of the ammonia treatment. In addition, the flesh sides of the skins are protected from the action of the ammonia, warmed concentrated ammonium hydroxide solution is used instead of steam to maintain the necessary degree of moisture in the chamber, the hides or skins and the gaseous or vaporous contents of the chamber are kept in relative movement and the unconsumed ammonia is expelled from the chamber by warm air or other warm gases which do not react with ammonia.

Chrome Tanning. Brit. Pat. 182,289. A. GLOVER and G. MARTIN, Manchester. May 26, 1921. A chrome-tanning liquor is obtained by reducing chromic acid from bichromates and sulphuric or hydrochloric acid by means of dried whey powder, prepared from waste whey produced in cheese manufacture. The solution of bichromate is stirred during the addition of acid, which in the case of sulphuric acid heats the liquor to boiling and the dried whey powder is added to the hot solution. The proportions of bichromate and acid are calculated so as to give the product $Cr(OH)SO_4$ or $Cr(OH)Cl_2$.

Preparation for Treating Leather. U. S. Pat. 1,407,449. R. E. TOMMERSON, St. Louis, Mo. Filed Oct. 23, 1920. A preparation for treating leather, comprising the following ingredients in substantially the following proportions by weight:

Trisodium phosphate 3¼ parts,
Sulphonated oil 2 parts,
Water.

Method of Making Leather Yarn and Article. U. S. Pat. 1,415,313. W. M. CAVANAUGH, New York, N. Y. Filed Oct. 15, 1918. A leather yarn comprising a core, and twisted, leather strips surrounding the same.

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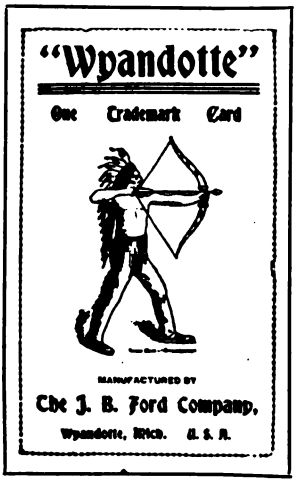

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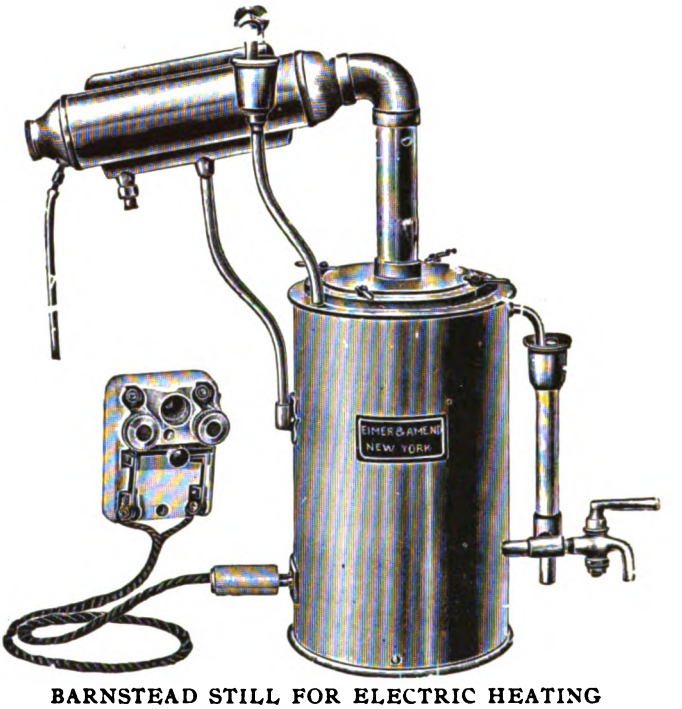

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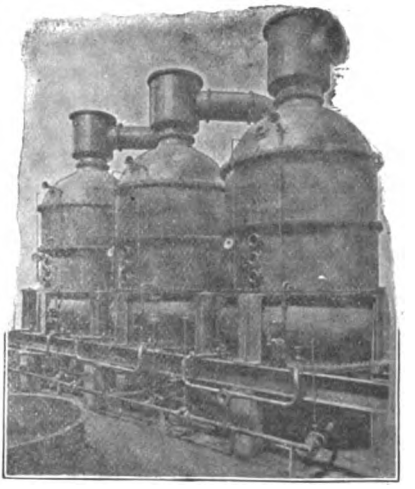

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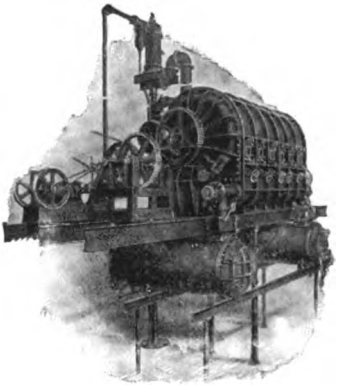

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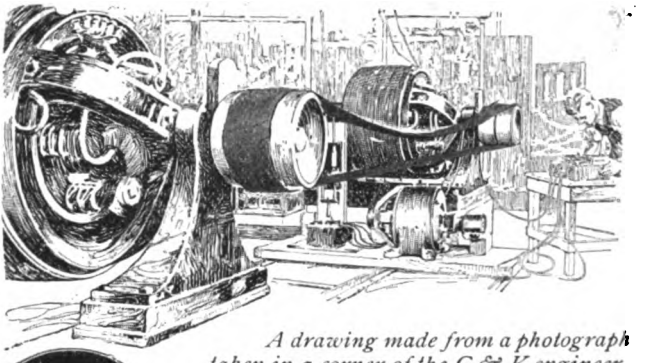

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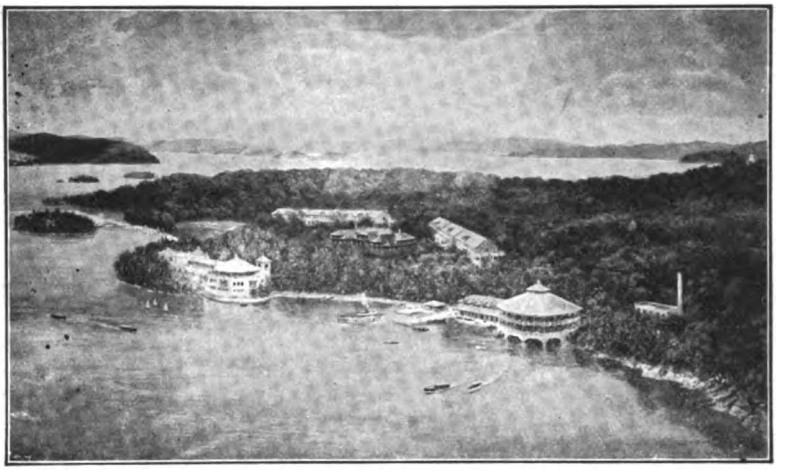

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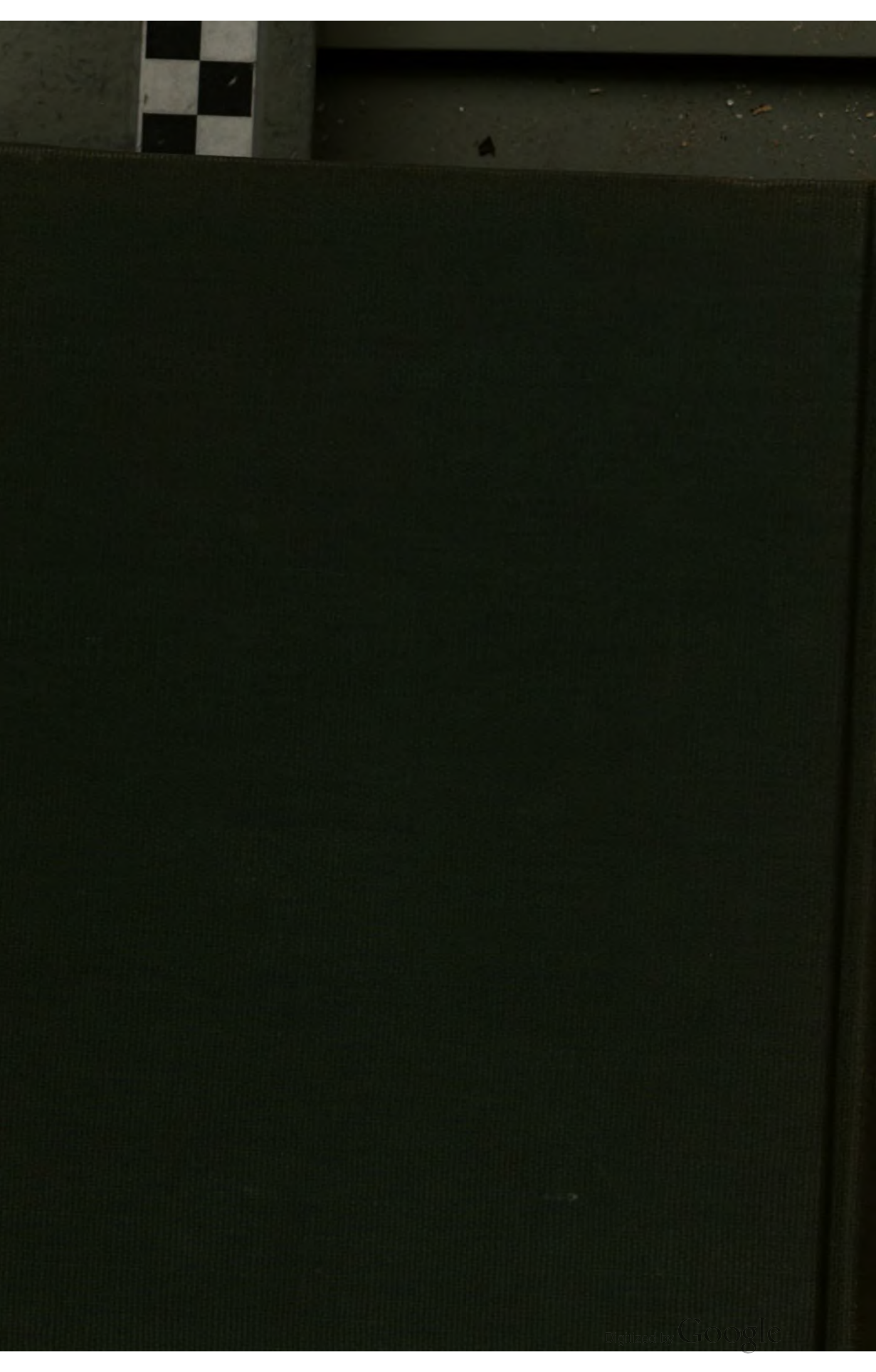
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